DOCUMENT RESUME

ED 206 895 CE 030 038

AUTHOR	Green, C. Paul; Burkhalter, Wayne
TITLE	Alcohol Fuel Production for Vocational Students: Secondary, Postsecondary.
INSTITUTION	Navarro Coll., Corsicana, Tex.
SPONS AGENCY	Texas Education Agency, Austin. Dept. of Occupational Education and Technology.
PUB DATE	81
NOTE	207p.
EDRS PRICE	MF01/PC09 Plus Postage.
DESCRIPTORS	*Agricultural Education; Agricultural Production; Behavioral Objectives; Chemistry; Curriculum; Curriculum Guides; Definitions; Economics; Engineering; *Fuels; *Learning Modules; Microbiology; Postsecondary Education; *Production Techniques; Secondary Education; *Vocational Education
IDENTIFIERS	*Alcohol Fuels

ABSTRACT

In order to help bring about the potential for alcohol production by the farming community, Navarro College (Texas) has developed this curriculum for secondary and postsecondary levels in alcohol fuel production. The alcohol fuel curriculum consists of five modules for use in practical hands-on vocational programs. The curriculum is designed to equip students to manage the alcohol production process. The modules contain a comprehensive bibliography, graphs, charts, and suggested resources for additional supportive documentation. Each unit also contains an introduction, objectives, a list of instructional materials needed, terms and definitions, information on the module topic, and a summary of the module. In addition, examples of suppliers of raw materials are included. Subjects covered in the five modules include alcohol fuel production economics, chemistry, microbiology, engineering, and agricultural production. (KC)

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ED206895

ALCOHOL FUEL PRODUCTION
for
Vocational Students
Secondary
Postsecondary

By

Project Director--C. Paul Green

Curriculum Development Specialist--Wayne Burkhalter

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Materials developed by
Navarro College
Corsicana, Texas

in cooperation with
Research Coordinating Unit
Department of Occupational Education and Technology
Texas Education Agency
Austin, Texas 78701

Project # 11230068

FIRST EDITION
1981

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PREFACE

The United States is facing one of its most challenging decades in recent history. Fuel supply and inflationary prices have forced us to consider alternate energy sources as a means of preserving our standard of living, industrial society, and economic stability. One such alternate fuel is gasohol. Presently, foreign crude oil provides the raw material for about one-half of the liquid fuel production in the U. S. Political instability in foreign oil-producing countries underscores the need to decrease our ever-growing dependency on foreign energy sources and to lessen our vulnerability to such imports. Gasohol as a liquid fuel can be used as a renewable domestic alternate energy source and to supplement our increasing appetite for petroleum.

The present farmer and agriculture student have neither the skills necessary to cope with the energy crisis we are now facing, or the increased problems predicted for the future. This condition reinforces the importance of alternative fuel curricula which will produce disseminatable data capable of making an immediate and long-range contribution to the farming community and to the national energy scenario by developing a skill knowledge that will impact the implementation of fuel alternative measures.

To help bring about the potential for alcohol production by the farming community, community colleges in rural settings (such as Navarro College) must make training opportunities in alcohol production and uses available to students in agriculture, welding, energy conservation, solar, physics, chemistry, biology, and related disciplines. Students must be taught to understand the global energy crisis and must be trained in the technical skills necessary to discover energy conservation measures, to monitor the use and expenditures of precious fossil fuels, and to integrate and adopt alternate sources into farm production.

Navarro College has developed for the Texas Education Agency a curriculum in Alcohol Fuel Production that can make an immediate contribution to our society. This alcohol fuel curriculum consists of five modules for use in practical hands-on postsecondary vocational programs. The curriculum is designed to equip students to manage the alcohol production process.

The modules contain a comprehensive bibliography, graphs, charts, and suggested resources for additional supportive documentation. In addition, examples of suppliers of raw materials are included as reference material.

ACKNOWLEDGMENTS

Throughout this project, many people and institutions have contributed greatly to the development and completion of the Alcohol Fuels Curriculum. First, this project owes a debt of gratitude to the staff of the Research Coordinating Unit, Texas Education Agency, whose support and encouragement made the project possible.

We extend thanks to those members who served on the Curriculum Development Committee and provided valuable input to module content and format:

Mr. Roger F. Stebbing, Marlboro Enterprises, Inc.

Mr. Samuel F. Eakin, Energy Research Group, Inc.

Dr. Charles C. Faust, III, L.S.U. at Eunice

Dr. M. M. Norris, East Texas State University

Mr. Oscar Millican, Research Consultant

Mr. Durwin Hohhertz, East Texas State University

The Project Director and Curriculum Development Specialist are also grateful for the efforts of the following individuals for helping write, edit, and illustrate the modules:

Mr. Durwin Hohhertz

Mr. Tom Hammargren

Mr. M. M. Norris

Mr. Carey Flowers

Mr. Jeremy Pereira

Mr. Charles Orsak

Mrs. Kay Garrett

Mrs. Norma Lewis

A special thanks goes to all the participants in the Navarro College Alcohol Fuel Production and Technology Workshops. Each participant gave special insight into the diversity of situations involved in producing alcohol fuel.

A final and wholehearted thanks to the Navarro College agriculture students who supplied enthusiasm, time, and labor to make the programs interesting and successful.

ALCOHOL FUEL PRODUCTION

MODULE I - ECONOMICS

I. Introduction:

Society is in transition from an economy that is dependent on oil to one utilizing alternative sources of fuel. In this day of high fuel costs, the farmer, industrialist and other users of gasoline and diesel must seek alternatives in order to reduce the cost of production for their products.

The production of fermentation ethanol is based on established technology, and a variety of raw materials is available from the agricultural sector. Fermentation ethanol can be produced from such crops as corn, wheat, sugarcane, potatoes, grain sorghum; from agricultural by-products and wastes; and from cellulose. Actually, whatever can be broken down to sugars can become primary material for fermentation. Thus, the variety of raw materials is quiet large. These crops, as well as distressed grains, are ideal for the production of fermentation ethanol.

The decision to turn energy crops into fuel for farm power and the country's autos may have a price-increasing effect on food prices. When gasoline reaches $2.00 per gallon, industry (U.S. distillers) could probably afford to pay $5.00 a bushel for corn. At $3.00 per gallon, the price of corn could easily go to $6.00 per bushel. This could certainly put pressure on increasing other related food prices. With these thoughts in mind, this module is designed to develop the tools needed to provide guidelines for making managerial decisions about the production of alcohol fuel.

II. Objectives:

Upon completion of this module, the student will be able to:

A. Explain why the use of alcohol for fuel could affect the price of food in the United States.

B. Identify terms and definitions related to the economics of alcohol production.

C. Explain the feasibility of producing alcohol by using crops which may be converted into fuel, and point out the factors and policies that determine whether a farmer may profit by producing these crops.

D. Discuss budgeting for crop production.

E. Discuss budgeting for ethanol production.

F. Point out the fixed and variable costs related to ethanol production.

G. Explain the value of stillage, a coproduct of ethanol production, as livestock feed.

H. Recognize capital and operational costs involved in ethanol production.

I. Demonstrate the ability to prepare a feasibility study which reflects both capital and operational costs of production of ethanol.

III. Instructional Materials:

A. Hand Calculator

B. Pencil

C. Paper

D. Basic Economic Reference: For Study of Economic Principles Used in Decision Making.

IV. References:

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MODULE I - ECONOMICS

Terms and Definitions:

1. Production Function--The technical relationship between the amount of resource or input used to produce a product and the corresponding output or yield of that product--input/output relationship.

2. Marginal--Incremental changes increases or decreases, which occur at the edge or margin (extra or additional can be a negative, positive, or zero amount).

3. Marginal Physical Product--The extra or additional production occurring as a result of using an extra unit of resource or input.

4. Law of Diminishing Returns--Operates as additional units of a variable input are used in combination with one or more fixed inputs, because the additional product being produced, per unit of added, variable, and input will eventually begin to decline.

5. Marginal Value Product--The amount added to total value product when another unit of the variable input is used.

6. Marginal Cost--The change in total cost when output is changed by one unit.

7. Marginal Revenue--The change in income, or the additional income received from selling one more unit of output.

8. The Decision Rule--Profit will be maximized when the marginal revenue is equal to marginal cost.

9. Input Substitution--Finding the least cost input.

10. Opportunity Cost--The income that could have been received if the input had been used in its most profitable alternative uses.

11. Fixed Costs--Costs incurred for those resources which do not change as output is increased or decreased.

12. Variable Costs--Those costs which increase or decrease as varying amounts of the resources are used to increase or decrease production.

13. Total Cost--The sum of the fixed costs and the variable costs.

14. Principle of Comparative Advantage--States that individual regions will tend to specialize in the production of those commodities for which their resources give them a relative or comparative advantage.

15. Budget--A summary of the income and expenses used to determine productivity of alternative uses of resources.

16. Cash Flow Budget--A summary of the cash inflow and cash outflow for a business over a given time period.

17. Balance Sheet--A systematic organization of everything "owned" and "owed" by a business or individual at a given point in time.

18. Solvency--Measures whether total assets are greater than total liabilities. If not, the business is insolvent, or technically, bankrupt.

19. Liquidity--Measures the ability to generate cash needed to meet cash obligations without seriously disrupting the production activities.

20. Net Worth--The result of assets minus liabilities.

MODULE I - ECONOMICS

OUTLINE

- I. Feasibility
  - A. Feedstock Economics
    - 1. Sugar Crops
    - 2. Starch Crops
    - 3. Cellulose
  - B. Factors and Policies
- II. Budgeting for Crop Production
- III. Budgeting for Ethanol Production
- IV. Fixed and Variable Costs
- V. Value of Stillage
- VI. Capital and Operational Costs
- VII. Summary

ALCOHOL FUEL PRODUCTION

MODULE I - ECONOMICS

I. Feasibility

A. Feedstock Economics

According to the U.S. Department of Agriculture, present yearly food consumption is approximately 1,600 pounds of grain eaten in the form of cereal products, meat, milk, and eggs, or the utilization of about .9 acres of cropland per person in the United States. According to Worldwatch Institute, the typical U.S. automobile (10,000 miles per year at 15 miles per gallon) will use 14,600 gallons of alcohol annually. Even if gasohol (10% alcohol, 90% gasoline) were used, this would require 1.460 pounds of grain, which would almost double the required acres needed from .9 acres to 1.7 acres. This estimate does not include any data concerning the utilization for alcohol. Three types of materials lend themselves readily to alcohol production. These materials are sugar crops and materials, starches, and celluloses. Each will have advantages and disadvantages. Usage will be determined by the individual.

1. Sugar crops and materials are crops with fermentable sugars present at harvest time. Sugar beets are available in some areas, while sugar cane predominates in others. Sugar crops require little preprocessing, no enzymes, and yield about 27 gallons of alcohol per ton. Sugar crops have disadvantages in the cost of production and long-term storage of the original materials.

2. Starches are corn, wheat, grain sorghum, and potatoes. The breakdown of starch into simple sugar is accomplished by fermentation. This may be done by using heat with enzymes, acid, and yeast. The amount of water present in the starch will greatly affect its breakdown to sugar. The more water present, the greater the ease of breakdown. A bushel (56 pounds) of corn, wheat, or milo is 60% starch and will yield about 2.6 gallons of alcohol. Corn and grain sorghum in particular have several advantages.

    a. Availability

    b. Ease of storage, and

    c. The waste material from fermentation, which provides nutritious feed for livestock.

3. The last raw material to be considered is cellulose (cotton, wood, paper, or crop residue). Acids (hydrochloric or sulfuric) and

enzymes from molds have the ability to ferment cellulose to alcohol. Cellulose is generally easier to break down when it is wet and green. Wet green plant material stores poorly and should be processed rapidly. Crop residue (corn stalks, straw, and grass) may also be used. One must consider the value of crop residue going back into the soil as further nutrients for the soil and as a preventer of erosion. It may be in the best interest to society to first protect its soil resource base.

B. Factors and Policies

The profitability of converting energy crops into ethanol is determined by factors and policies which provide a workable index in evaluating a farmer's success as a manager. Recognizing that profits by themselves may not be the sole objective of an individual farmer, he/she, nevertheless, needs to know what effect decisions will have on income in order to make rational decisions.

Individual decision making is a highly complex and personal process. There are tools or aids available to the individual that can improve decision making. First, however, one must develop the skills necessary to use these tools. This involves the reasoning process itself.

The formation of ideas is largely deductive. That is, we reason from certain known information to a tentative conclusion, an idea. After doing this, information is collected to test the idea. This is empirical evaluation, the testing of an idea by observing specific evidence. We all unconsciously use both processes in arriving at our conclusions. By converting these thought processes from the unconscious to the conscious, most people can improve their effectiveness. They become more systematic in their thinking. This systematic process, known as the scientific method, has been shown by experience to be the most effective means of investigating a problem.

Economic principles that have been developed over the years constitute an important tool to be used in deductive reasoning. These principles indicate what type of information we need to collect and study.

Historical information records on the internal observation of the farm business may be a valuable source of information for decision making.

The budget and simulation procedures are testing devices. By use of such techniques it is often possible to compare farming alternatives on paper before committing the dollars required to put the idea into practice.

The preceding tools and techniques are helpful in analyzing options available and in estimating the consequences of alternative lines of action when outcomes can be predicted with some accuracy; principles, budgets, and records can be used.

II. Budgeting for Crop Production

In determining the economic feasibility of producing crops for processing and producing alcohol, the cost and returns must be considered for the alternative uses of the crop under consideration. The basic production intent will be determined by an individual's need for energy self-sufficiency based on the current availability based on the cost of alternative sources. Tables 1 and 2 on the following pages give examples of a budget form that may be used in determining the costs incurred in the production of grain sorghum and wheat, respectively, using custom harvest. You will note that a column is available for your use in making adjustments for price changes and technological improvements. The same type of form can be used for any of the inputs that may be used for ethanol production.

TABLE 1

GRAIN SORGHUM PRODUCTION COSTS

OPERATING INPUTS:	UNITS	PRICE	QUANTITY	VALUE	YOUR VALUE
Grain Sorghum Seed	lbs.	.50	5.0	2.50	___
Nitrogen (N)	lbs.	.18	70.0	12.60	___
Phosphate (P_2O_5)	lbs.	.16	60.0	9.60	___
Potash (K_2O)	lbs.	.075	40.0	3.00	___
Insecticide	acre	4.50	.33	1.48	___
Herbicide	acre	8.00	1.0	8.00	___
Rent Fertilizer Spreader	acre	1.45	.5	.72	___
Custom Combine	acre	12.00	1.0	12.00	___
Custom Hauling	cwt.	.22	30.0	6.60	___
Tractor Fuel and Lube	acre			3.12	___
Tractor Repair Cost	acre			2.77	___
Equipment Fuel and Lube	acre			.26	___
Equipment Repair Cost	acre			2.66	___
TOTAL OPERATING COST				65.32	___
CAPITAL COST:					
Annual Operating Capital		.09	17.919	1.61	___
Tractor Investment		.09	42,482	3.82	___
Equipment Investment		.09	30.404	2.74	___
TOTAL INTEREST CHARGE				8.17	___
OWNERSHIP COST:					
(Depreciation, Taxes, Insurance)					
Tractor	hr.			5.27	___
Equipment	hr.			4.84	___
TOTAL OWNERSHIP COST				10.11	___
LABOR COST:					
Machinery Labor	hr.	2.5	2.675	5.69	___
TOTAL LABOR COST				6.69	___
PRODUCTION:					
Custom Harvest	cwt.	___	30.0		___

TABLE 2

WHEAT PRODUCTION COSTS

OPERATING INPUTS:	UNITS	PRICE	QUANTITY	VALUES	YOUR VALUE
Wheat Seed	bu.	4.00	1.0	4.00	
18-46-0 Fertilizer	cwt.	10.55	1.0	10.55	
Nitrogen (N)	lbs.	.22	40.0	8.80	
Insecticide	acre	2.50	1.0	2.50	
Custom Combine	acre	9.20	32.0	9.20	
Custom Hauling	bu.	.10	2.0	3.20	
Fertilizer Spreader (Rent)	acre	1.45	2.0	2.90	
Tractor Fuel and Lube	acre			2.29	
Tractor Repair Costs	acre			1.74	
Equipment: Fuel and Lube	acre			.76	
Equipment: Repair and Cost	acre			2.14	
TOTAL OPERATING COST				48.08	
CAPITAL COST:					
Annual Operating Capital		.10	21.071	2.11	
Tractor Investment		.10	28.53	2.85	
Equipment Investment		.10	15.207	1.52	
TOTAL INTEREST CHARGE				6.48	
OWNERSHIP COST: (DEPRECIATION, TAXES, INSURANCE)					
Tractor	hr.			3.72	
Equipment	hr.			2.42	
TOTAL OWNERSHIP COST				6.13	
LABOR COST:					
Machinery Labor	hr.	2.0	2.271	4.54	
Other Labor	hr.	2.0	.40	.80	
TOTAL LABOR COST			2.671	5.34	
PRODUCTION:					
Custom Harvest	bu.		32		

TABLE 3

FUEL USE IN CROP AND LIVESTOCK PRODUCTION

Use these average fuel requirements as budgeting guides, keeping in mind that your actual fuel usage can be as much as 50% higher or lower, depending on operating conditions.

FIELD OPERATIONS	Diesel gal/a.
TILLAGE	
Moldboard plow	
Light soil	1.05
Medium soil	1.90
Heavy soil	2.80
Chisel plow	1.05
Heavy disk	1.40
Standard disk	
Plowed soil, 1st time over	.70
Plowed soil, 2nd time over	.50
Spring tooth harrow	.50
Spike tooth harrow	.28
Field cultivator	.70
PLANTING	
30 inch rows	.56
Grain drill	.35
Potato planter	1.05
Transplanter	1.28
CULTIVATION	
Row crops, first cultivation	.42
Row crops, second cultivation	.35
Rotary hoe	.21
HARVESTING OPERATIONS	
Cutterbar mower (pto)	.35
Mower conditioner (pto)	.70
Windrower, self-propelled	.70
Hay rake	.20
Baler, hay	1.05
Baler, straw	.77
FORAGE HARVESTER (FLAIL)	
Green chop	2.45
FORAGE HARVESTER (CYLINDER AND FLY WHEEL TYPES)	
Haylage	1.75
Dry hay or straw	1.05
Row crop 30 in. rows	2.30
COMBINE HARVESTER	
Small grain	1.05
Soybeans	1.20
Corn, 30 in. rows	1.47
COMBINE PICKER	
40 in. rows	.91
30 in. rows	.98
PICKER SHELLER	
40 in. rows	1.05
30 in. rows	1.26
Potato harvester	1.68
MISCELLANEOUS	
Row crop sprayer	.14
Fertilizer spreader, bulk spinner	.21
Anhydrous ammonia applicator	1.19
FORAGE BLOWER	
Haylage or corn silage	1.75
Dry hay or straw	.70

TABLE 3 (CONT'D)

CROPPING SYSTEM	Diesel gal/a.
Corn - conventional method	6.85
Corn - plowing with minimum tillage planting	5.40
Corn - no plowing minimum tillage planting	4.30
Corn harvested and stored as whole plant silage conventional methods	8.65
Plowing with minimum tillage	7.20
No plowing, minimum tillage	6.10
Soybeans - conventional method	6.50
Small grains - oats, barley, wheat	3.00
Small grains - with plowing	4.70
Hay - dry cured, 3 cuttings, baled	8.65
Haylage	
3 cuttings or dry chopped	13.00
Using combined type cutting with self-propelled, cut crush, windrow	
Hay - 3 cuttings	5.20
Haylage - 3 cuttings	9.50

GRAIN SORGHUM - PRODUCTION

Conventional till	
Plow	1.53
Tandem disk	.51
Springtooth	.41
Plant	.32
Spray	.10
Cultivate	.35
Combine	1.00
	4.22

MINIMUM TILL

Disk	.51
Spray	.10
Plant	.32
Cultivate	.35
Combine	1.00
	2.79

TABLE 3 (CONT'D)

HARVESTING

SYSTEM 1 - HAY BALING

Mow 7'	0.46
Rake	0.40
Bale pto, standard	0.73
Total Gal	1.59

SYSTEM 2 - HAY BALING

Mow 7"	0.46
Rake	0.40
Bale pto. Large roll	0.80
Total Gal.	1.66

SYSTEM 3 - HAY BALING

Swath 14' SP	0.40
Bale pto, Standard	0.73
Total Gal.	1.13

SYSTEM 4 - HAY BALING

Swath 14' SP	0.40
Bale pto, large roll	0.80
Total Gal.	1.20

SYSTEM 5 - HAYLAGE

Swath 14' Sp	0.40
Forage harvester	3.00
Total Gal.	3.40

SYSTEM 6 - LOOSE HAY

Mow 7"	0.46
Rake	0.40
Loose hay stacker - 3 ton	1.50
Total Gal.	2.36

SYSTEM 7 - LOOSE HAY

Swath 14' SP	0.40
Loose hay stacker - 3 ton	1.50
Total Gal.	1.90

1 BASED ON HAY CUTTING 1-1/4 TONS PER ACRE. HAULING NOT INCLUDED EXCEPT HAYLAGE.

HAULING

	Gasoline First Mile	gal/a. added Each Mile
Corn silage, haylage	2.0	.5
small grain, shelled corn	.5	.2
Baled hay, straw, etc.	.5	.2

TRACTORS

	Gallons per hr.	
HORSEPOWER	Gasoline	Diesel
20	1.3	.9
30	2.0	1.4
40	2.7	1.8
50	3.3	2.3
60	4.0	2.8
70	4.7	3.2
80	5.3	3.7
90	6.0	4.2
100	6.7	4.6

TABLE 3 (Contd.)

50-COW DAIRY HERD

	kwh/year
Bucket milker	3,000
Bucket milker plus transfer system	4,000
Pipeline or Parlor	5,500
Automatic takeoff (two levels of vacuum)	10,000
Silo unloader	1,800
Feed Conveyer	800
Bunk feeder	600
Barn cleaner	500
Manure staker	400
Mechanical scraper	6,600
Crowd gate	150
Roller mill	300
Hammer mill	750
Well pump	1,600
Automatic takeoff (electronic)	7,500
	Gasoline gal./year
Feed grinding and mixing	90
Manure scraping	180
Manure loading	38
Manure spreaking	138
Liquid manure pumping and agitating	180
Trench silo unloading with front-end loader	120
Self unloading wagon	180
Mixer wagon	300
Paster work	2/acre

Multiply diesel fuel usage by 1.4 to convert to gasoline usage and by 1.7 to convert to LP-gas usage. Multiply gasoline usage by 0.72 to convert to diesel and by 1.2 to convert to LP-gas usage.

III. Budgeting for Ethanol Production

In determining the number of gallons of fuel alcohol needed per year it is necessary to plan the production program, considering crops, acres, size, and kind of fuel being used. Table 3, Fuel Use in Crop and Livestock Production, from Doane's Agricultural Report, gives the average fuel requirements for the production of farm crops. With this information as a budgeting guide, the operator can then estimate one's fuel requirements.

Thus, the cost of producing the crop and the gallons of fuel required can now be computed. By determining the gallons of yield per acre of alcohol, bushels per acre times gallons of alcohol per bushel equals gallons per acre (Table 4) and by dividing the cost per acre by the gallons per acre, the crop cost per gallon is determined. Referring to Table 1, Grain Sorghum Production Costs, total cost of producing a bushel of grain sorghum (using the assumed costs) would be $1.69 per bushel. Each bushel of grain sorghum will produce approximately 2.6 gallons of ethanol, and 16.8 pounds of residue of approximately 33% protein content (Table 4).

TABLE 4
Gallons of Ethanol and Coproduct Produced

Raw Material*	Gal. of ethyl alcohol /unit	Coproduct Produced (lb/unit)	% Protein of Coproduct
Wheat (bu)	2.6	20.7	32
Corn (bu)	2.6	16.8	27
Sorghum (bu)	2.6	16.8	33
Potatoes (cwt)	1.4	14.8	10
Sugar Beets (ton)	20.3	264	10

*Based on grains containing 14% moisture; potatoes, 75% moisture.

Thus, with a production cost of grain sorghum of $1.69 per bushel divided by 2.6 gallons production of ethanol per bushel, the raw material cost for ethanol is sixty-five cents per gallon ($1.69 ÷ 2.6 = .65).

When one is considering which raw materials to use, the following questions should be answered:

1. What is available in the immediate area?
2. What crops can be grown to maximize production?
3. What wastes are available?
4. How many gallons of fuel alcohol per year is needed?
5. What is the yield of alcohol per ton or bushel of raw material?
6. How many days per year will the plant be operated.
7. How many gallons per day will be produced?
8. What energy source will be used to operate the plant?
9. What alternatives are there for the utilization of the residue?
10. Will additional storage facilities be needed?

These questions may not be all that confront the individual who ponders the decision as to value comparisons of selling the crops, or converting them into ethanol for fuel.

The determination of the available crops in the immediate area would perhaps be the least difficult of all the questions. An individual could observe the crops being grown and determine this answer.

Records, experiment station data, and local comparisons can help determine those crops that will maximize production. Certainly consideration must be given to the potential alcohol production derived from the crops under consideration.

Waste material that could be considered for alcohol production under certain conditions would be primarily determined by the kind of enterprises in the area. Care and consideration should be given in using crop residue, corn stalks, cotton stalks, etc., relative to possible erosion and soil nutrient replacement.

IV. Fixed and Variable Costs

Investment and costs of operation are not well established. Capital costs, the purchase of the plant and equipment, is the largest item of expenditure for the ethanol production venture. However, unless this cost is borne entirely by the owner's equity or unless phenomenally bad loan terms are obtained, this entire cost is not borne in the first or any single year of operation. The capital cost is the sum of the payments made during the year.

EXAMPLE:

Minimum investment in facilities is probably around $25,000. For example, one expert estimates an investment of about $34,000 in a plant having the capacity to handle and distill 100 bushels of corn per batch each week. Each batch would produce 260 gallons of ethanol for an annual capacity of 13,500 gallons. Figuring all fixed and variable costs: grain production, 5,200 bushels at $1.69 per bushel, distillation cost (depreciation, fuel, labor and additives) at $2.52 per bushel.

$1.69 x 5,200 = $8,788.00

$2.52 x 5,200 = 13,104.00

Total $21,892.00 ÷ $1.62 per gallon

If drying operation must be added for the coproducts, an additional cost must be calculated--perhaps as much as 40 cents per gallon. The capital cost will be dependent upon the size of the loan obtained, the period of time for repayment, the interest ratio, and the frequency of payments.

Aside from costs, considerable time and skill are required to operate an efficient facility. It is estimated that employment on the farm plant will require the operator to spend at least two 2-hour periods each day the facility is in operation. Rather close supervision is required during certain phases of operation.

The cost of equipment can only be estimated after a maximum plant size has been established by determining the individual's needs. Then this equipment cost must be compared to financial capability. If the cost of equipment is within acceptable range, the cost of operations can be determined. The cost of financing is computed by using current money market conditions and the requirements for borrowing as a function of financial capability.

If the equipment cost exceeds the individual's financial capability, the plant size must be scaled down until a match is achieved. Once an appropriate plant size is determined, the other two cost factors are computed. If the cumulative production cost (which results by summing the per-gallon cost contribution of each factor) is greater than the anticipated price of alternative fuel minus the value of the stillage, the project is implausible and no further effort should be expended.

The basic production intent defines a range of plausible production capacities. If the principle intent is energy self-sufficiency, then the level of production should be matched to current personal objective and the financial capabilities of the prospective producer. Other potentially limiting factors are the availability of fuel in contrast to the amount required, the availability and cost of required quantities of feedstock, the availability of utilities like water, electricity and sewer, and the availability of chemicals and supplies.

The availability of operating labor and the cost of automation pose a trade-off that is resolved as a function of the availability of money to buy equipment (capital equipment budget), or the availability of cash generated by operations (operating capital). If a qualified labor pool is readily and inexpensively available and if the capital equipment budget is tight, it is logical to opt for a minimum of automation. In contrast, if the operating cash flow is very near its upper limit and the capital equipment budget will allow, automatic equipment may be purchased to conserve operating capital.

V. Value of Stillage

Stillage coproduct of ethanol production is of value as livestock feed. Stillage feed value varies from animal to animal although feeder cattle and dairy cattle are consistently the most appropriate for using the coproduct. Fortunately, there is a long history of feeding animals with the grain stillage produced by major distilleries. Volumes of data have been compiled from studies and tests sponsored by the distillers Feed Research Council in Cincinnati, Ohio 45202. The results of these tests give relative stillage feed values for a broad variety of animals, including dogs, horses, chickens, turkeys, hogs, cattle, and humans.

Stillage is usually used as a protein supplement to feed rations. As such, its value can be approximated by comparison to the least expensive available protein source in the area. Then adjustments should be made to reflect the advantages or disadvantages that stillage may have over the least expensive competing product available.

This is based on dry matter basis. If alfalfa at 20% protein is available to a feeder at a price of $120 per ton, this price can be converted to a protein basis by determining the number of pounds of protein in a ton of this hay and dividing the cost by that number.

EXAMPLE: 2000 lbs. hay x .20 = 400 lbs. protein per ton, and $120 per ton ÷ 400 lbs. protein per ton of hay = $0.30 per lb. protein.

Thus, an equivalent protein basis of the stillage value can be calculated. If the stillage is 30.6% protein, a ton of stillage contains 612 pounds of protein. 612 lbs. protein x .30 = $183.60 per ton of stillage.

It is important to remember that the value derived in this fashion is only a minimum probable value. If the stillage is sold, the price a person actually obtains from the sale is its actual value. If it is fed, the actual value is the value of feed not purchased.

Effective use of the coproduct, distiller's mash (wet stillage) or some form of the coproduct is practically a must if on-farm ethanol production is to be feasible. It is estimated that the value of distillers' mash will reduce the cost of producing ethanol by about 40 to 45 cents per gallon.

When stillage is dried, an excellent protein source is provided for cattle. The protein content of dried grains may be twice as valuable as that of soybean meal. Nebraska nutritionists calculated that dry distillers grains are worth as much as 68% of the value of the original grains for feeding.

Due to the cost of drying, it is likely that farmers will want to feed the product wet. However, much less is known about feeding wet stillage, and its high moisture presents some feeding problems.

For every bushel of corn or grain sorghum used in distillation, more than 200 pounds of wet stillage may be produced. Table 5 indicates the relationship of wet stillage to dry distillers' grains.

TABLE 5
Nutrient Content of Distillers' Grains[1]

	Wet Stillage (as fed)	Dry Matter Basis
Dry Matter (%)	6.2	100.0
Crude Protein (%)	1.9	30.6
TDN (%)	4.2	87.1
Metabolizable Energy (Mcal per lb.)	0.7	1.10

[1] Doans Agricultural Digest

Of the 200 pounds, only 12.4 pounds of the total weight is dry matter. In order to consume one pound of dry matter, an animal would have to eat or drink about 2 gallons of wet stillage.

Without treatment, the material spoils rapidly, so it must be fed as it comes from the still. A guide determining the number of animals needed to consume the stillage has been determined. For example, a mature cow can consume the stillage that results from producing 1 gallon of ethanol daily; a feeder calf, stillage from about 0.7 gallons of ethanol production; and a hog, stillage from about 0.4 gallons of ethanol.

When wet stillage is fed, the manure and urine volume tends to increase, and it has a laxative effect. The feeding value is somewhat limited for swine and poultry because of a deficiency of essential amino acids.

Handling and feeding methods to reduce problems are being studied. Treating wet stillage with propionic acid or other inhibitors prevents mold. Infusing ammonia or carbon dioxide into the material is effective, but an airtight container is needed.

It is possible to ensile stillage by adding ammonia or lime to reduce its acidity. Another technique is to use wet stillage to reconstitute dry forage or grain before storing in the silo. Some adjustment of ph will probably be required, however. Systems for reducing the moisture content of stillage from on-farm units may be developed that will prove to be economical.

Until progress is made in handling, storing, and feeding, farm still operators probably should plan to feed whole stillage mixed into complete beef or dairy rations.

VI. Capital and Operational Costs

Once the considerations for equipment selection are completed, the capital and operating costs may be estimated. The capital cost considerations are:

A. Equipment

B. Real estate and buildings

C. Permits and licenses

D. Availability of financing

In addition to capital costs, the operational costs associated directly with ethanol production must be calculated and charged against the value of the alcohol fuel and stillage. Among the costs of operation associated with ethanol production are:

A. Raw material, costs, feedstocks

B. Labor costs

C. Cost of fuel

D. Cost of chemicals and supplies

E. Cost of utilities

F. Cost of money

G. Cost of insurance

H. Cost of delivery

I. Cost of storage

J. Administrative expenses

The final decision to produce ethanol is the result of examining all associated concerns at successively greater levels of details. Initially, a basic determination of feasibility must be made and its results are more a "decision to proceed with further investigation" than an ultimate choice to build a plant or not. This initial evaluation of feasibility is performed by examining:

A. The total market (including on-farm uses and benefits) for the ethanol and coproducts.

B. The actual production potential.

C. The approximate costs for building and operating a plant of the size that appropriately fits the potential market and the production potential.

D. The potential for revenues, savings, or indirect benefits.

E. Personal financial position with respect to the requirements for this plant.

There are several points during the course of this evaluation that result in a negative answer. This does not necessarily mean that all approaches are infeasible. Retracing a few steps and adjusting conditions may establish favorable conditions; however, adjustments must be realistic not overly optimistic. Similarly, completion of this exercise with a positive answer is no guarantee of success, it is merely a preliminary investigation. The real work begins with specifics.

VII. Summary

Economics is concerned with the allocation of scarce resources to maximize benefits, choosing among competing wants. There are a few basic concepts, such as allocation, scarcity, goals, and time. This module has attempted to employ applicable economic tools to assist the student in the establishment of goals which may go beyond economics into value judgments.

This module on economics should enhance the student's understanding of the meaning of cost in all its many aspects. Thus, by pursuing one's own interest, one will promote that of society more effectually.

ALCOHOL FUEL PRODUCTION

MODULE II - CHEMISTRY

I. Introduction:

Because ethanol production is a process which involves chemistry, an understanding of the fundamentals of chemistry can increase one's chances for success in alcohol production. Furthermore, a knowledge of some basic chemical principles can be rewarding in itself since the process that is actually taking place in the containers of an alcohol plant is becoming of greater interest to growing numbers of people.

II. Objectives:

Upon completion of this module, the student will be able to:

A. Identify terms and definitions related to the chemistry involved in alcohol fuel production.

B. Define mass and matter in relation to weight, and demonstrate the ability to convert from one to the other.

C. Describe the three physical states or forms of matter.

D. Explain physical and chemical changes.

E. List the physical and chemical properties of matter.

F. Define latent heat of fusion in relation to heat capacity.

G. Point out how to interchange Fahrenheit and Celsius.

H. Recognize the chemical symbols for carbon, hydrogen, oxygen, and nitrogen.

I. Point out the difference between reactants and products as shown by a chemical equation.

J. Define molecule and atom.

K. Point out the relative atomic weights of hydrogen, oxygen, carbon, and nitrogen, and calculate the molecular weights of molecules containing only those elements.

L. Define mole in relation to the number of atoms represented.

M. Calculate the theoretical yield of ethanol from a given equation.

N. Explain the difference between a mixture and a solution.

O. Give examples of volume, density, and specific gravity, and how these are measured.

P. Describe the concept of acids and bases, explain acid-base neutralization, calculate the acidity of a mixture (pH), and explain the use of acid-base indicators and the pH meter.

III. Instructional Materials:

A. pH Paper

B. Litmus Paper

C. Thermometers: Fahrenheit, Celsius

D. Graduated Cylinder

E. Triple Beam Balance

F. pH Meter

G. Hydrometer

IV. References:

A. Newell, Sydney B., Chemistry - An Introduction 2nd ed., Little, Brown and Company, 1980.

B. Brown, Theodore L. and LeMay, Jr., H. Eugene, Chemistry - The Central Science, 2nd ed., Prentice-Hall, Inc., 1981.

C. Hawley, Gessner G., The Condensed Chemical Dictionary, 9th ed., Van Nostrand Reinhold Company, 1977.

D. Dean, John A., ed, Lange's Handbook of Chemistry, 12th ed., McGraw-Hill Book Company, 1979.

E. Weast, Robert C., CRC Handbook of Chemistry and Physics, 60th ed., CRC Press, Inc., 1979.

MODULE II - CHEMISTRY

Terms and Definitions:

1. Mass - The property of a body that is a measure of its inertia, that is commonly taken as a measure of the amount of material it contains and causes it to have weight in a gravitational field.

2. Matter - Material substance that occupies space and has weight.

3. Calibrated - Marked with gradations; e.g., a thermometer or a beaker.

4. Density - The mass of a substance per unit volume.

5. Enzyme - Any of numerous complex proteins that are produced by living cells and catalyze specific biochemical reactions at body temperature.

6. Reactant - A substance that enters into and is altered by a chemical reaction.

7. Fusion - A merging of elements into a whole.

8. Latent - Hidden; not active.

9. Fermentation - A chemical change with effervescence, an enzymetically controlled breakdown of an energy rich compound such as a carbohydrate to carbon dioxide.

10. Molecule - The smallest particle of a substance, composed of one or more atoms.

11. Mole - Also mol, short for molecular weight.

12. Neutralize - To make chemically neutral, neither acid or base.

13. Catalyst - A substance (e.g., an enzyme) that initiates a chemical reaction and makes it possible to proceed at lower temps than otherwise possible.

MODULE II - CHEMISTRY

OUTLINE

I. Mass and Matter

II. Physical States of Matter

III. Physical and Chemical Changes

IV. Physical and Chemical Properties

V. Latent Heat of Fusion; Heat Capacity

VI. Temperature

VII. Chemical Symbols

VIII. Chemical Reactions and Equations

IX. Molecules and Atoms

X. Atomic Weights and Molecular Weights

XI. Moles

XII. Theoretical Yield

XIII. Mixtures and Solutions

XIV. Volume, Density, and Specific Gravity

XV. Acids and Bases

    A. Concept of Acids and Bases

    B. Acid-Base Neutralization

    C. Units of Acidity; pH

    D. Acid-Base Indicators; pH Paper

    E. pH Meters

ALCOHOL FUEL PRODUCTION

MODULE II - CHEMISTRY

I. Mass and Matter

Every object or substance is made of matter, which is something which takes up space and requires energy to move it from one place to another. The constant amount of matter that an object has is called its mass. Therefore, mass is a measure of distance. The mass of an object is closely related to its weight and in fact, mass is actually measured by determining the weight of an object. (Weight is the mathematical product of mass times acceleration such as the acceleration of gravity.) For the purposes of alcohol production, the terms "mass" and "weight" are used interchangeably.

The units of mass of a weight which are used most commonly in alcohol production are the gram, kilogram, ounce and pound.

1 gram (g) = 0.002205 # pound (lb)

1000 gram (g) = 1 kilogram (kg)

16 ounce (oz) = 1 pound (lb)

1 pound (lb) = 453.6 gram (g)

Frequently, it is necessary to convert from one unit or dimension to another. Suppose you are directed to add 8 ounces of enzyme to your mash and your only measuring device is a balance pan which is calibrated in grams. Here 8 ounces is to be converted to grams so that the appropriate number of grams of enzymes can be weighed out. The calculation could look like:

$$8\ \cancel{\text{ounces}} \times \frac{1\ \cancel{\text{pound}}}{16\ \cancel{\text{ounces}}} \times \frac{453.6\ \text{grams}}{1\ \cancel{\text{pound}}}$$

$$= \frac{8 \times 1 \times 453.6}{16 \times 1}\ \text{grams}$$

$$= 226.8\ \text{gram}$$

Thus 226.8 gram is equivalent to 8 ounces and 226.8 grams of enzymes should be weighed out on the balance pan. Note that 226.8 gram equals 0.2268 kilogram.

II. Physical States of Matter

Matter exists in three states: gas (or vapor), liquid, and solid. SEE FIGURE 1.

A. A gas takes the shape and volume of the container to which it is introduced. Gas can be squeezed or compressed into a smaller container or allowed to expand into a larger container. Air is a mixture of gases. Carbon dioxide, which is a by-product of alcohol production, is a gas. During the process of distillation, water and ethanol exist for a time as gases.

B. A liquid has no specific shape of its own but does have a specific volume. These qualities mean that a liquid will assume the shape of the container but will not expand to fill the container as gases do. Rather, the top surface of a liquid will remain flat. Water is a liquid as is ethanol.

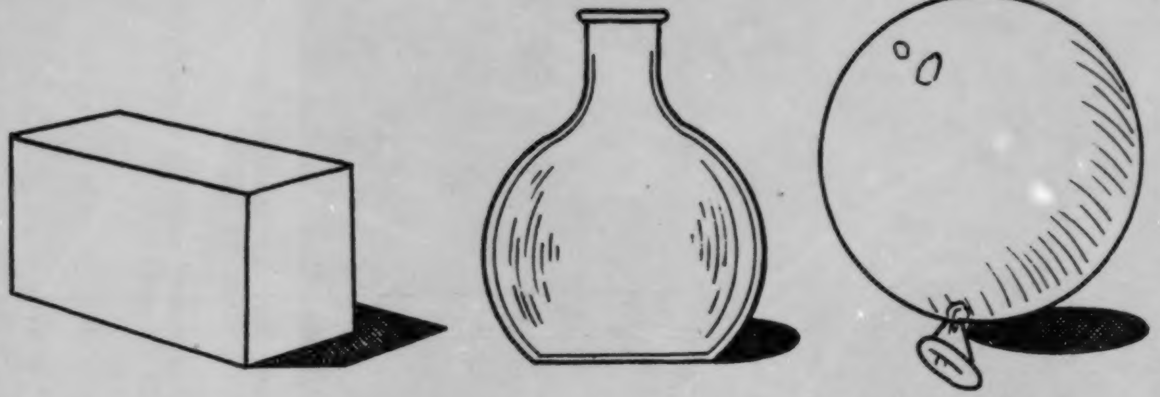
C. A solid has a rigidity not found in gases or liquids. A solid has a specific shape and volume. Solids and liquids cannot easily be compressed. Wood and granulated sugar are examples of solids.

III. Physical and Chemical Changes

Many substances can exist in more than one physical state. Liquid water, if cooled sufficiently, will freeze into a solid commonly called ice. If liquid water is heated sufficiently, it will boil, changing into a gas known as steam. These changes from one physical state to another are examples of physical changes. That is, there is a change in matter with no change in the composition of the matter. Whether the water is in the liquid, solid, or gas state, the chemical composition of the water is unchanged--it is still water. If, however, a solid enzyme is heated, it will not turn to a liquid enzyme and then to a gaseous enzyme but rather will decompose--its chemical nature will be altered. A chemical change will occur. When a chemical change occurs, the composition of a substance changes. If ethanol is ignited, a chemical change occurs in which ethanol burns in air to yield two new substances--carbon dioxide and water vapor.

IV. Physical and Chemical Properties

The concepts of physical changes and chemical changes are closely related to those of physical properties and chemical properties. A physical property of a substance are those properties (such as melting point, boiling point, density, color, specific heat) that can be measured with a change in composition of the substance. On the other hand, a chemical property of a substance describes how that substance reacts with or changes into other substances. For instance, a chemical property of ethanol is that it will burn in air, whereas a chemical property of water is that it will not burn in air. Examples of chemical properties are whether or not a substance will: react with water, react with air, burn, explode, support combustion, or act as a poison.



SOLIDS HAVE A DEFINITE SHAPE, OCCUPY A SPECIFIC VOLUME, AND ARE RIGID.

LIQUIDS OCCUPY A SPECIFIC VOLUME AND TAKE ON THE SHAPE OF THEIR CONTAINER. THE LIQUID SURFACE IS PERPENDICULAR TO A RADIUS DRAWN FROM THE CENTER OF THE EARTH.

GASES EXPAND TO FILL THE VOLUME OF THEIR CONTAINER. THE PRESSURE, TEMPERATURE, AND VOLUME OCCUPIED BY THE GAS SERVE TO DEFINE ITS DENSITY.

FIGURE 1

V. Latent Heat of Fusion; Heat Capacity

Application of heat to a container of pure liquid water at sea level will allow the water to absorb some of the heat. This will, quite understandably, raise the temperature of the water. If enough heat is absorbed by the sample of water the temperature will rise to a maximum of 212°F (100°C), but will permit continued boiling. Why doesn't continued heating cause a rise in temperature? Once the water temperature reaches 212°F, the water boils - converting liquid water at 212°F to water vapor at 212°F. Whenever a liquid is converted into a vapor (gas), heat is required. More specifically the amount of heat necessary to cause a phase change from liquid to gas at a constant pressure and temperature is called the latent heat of vaporization or merely the "heat of vaporization." This quantity is a physical property of a substance and differs from one substance to another. For example, the heat of vaporization of water approximately 540 calories/gram (972 Btu/lb) and of ethanol is only 204 calories/gram (367 Btu/lb). Thus more heat is required to vaporize a pound of water than is necessary to vaporize a pound of ethanol.

The common units of heat measurement are the calorie and the British Thermal Unit or Btu. One calorie is the quantity of heat required to raise the temperature of one gram of water from 15°C to 16°C. A Btu is the quantity of heat necessary to warm one pound of water from 30°F to 40°F. A conversion factor to use in changing units to Btu from calories or to calories from Btu is:

$$1 \text{ Btu} = 252 \text{ calories}$$

Thus if the heat of vaporization of water is 540 cal/gram, this value converted to Btu/lb would be:

$$\frac{540 \text{ cal}}{\text{gram}} \times \frac{1 \text{ Btu}}{252 \text{ cal}} \times \frac{453.6 \text{ gram}}{1 \text{ lb}} = 972 \frac{\text{Btu}}{\text{lb}}$$

Thus, in the example of boiling water, the continued addition of heat is causing not a temperature increase but rather a phase change from liquid to vapor (steam). SEE FIGURE 2.

Question: How many Btu are required to convert 150 gallons of water at 212°F to steam at 212°F?

Answer: Gallons of water must be converted to pounds of water before the Btu's are calculated.

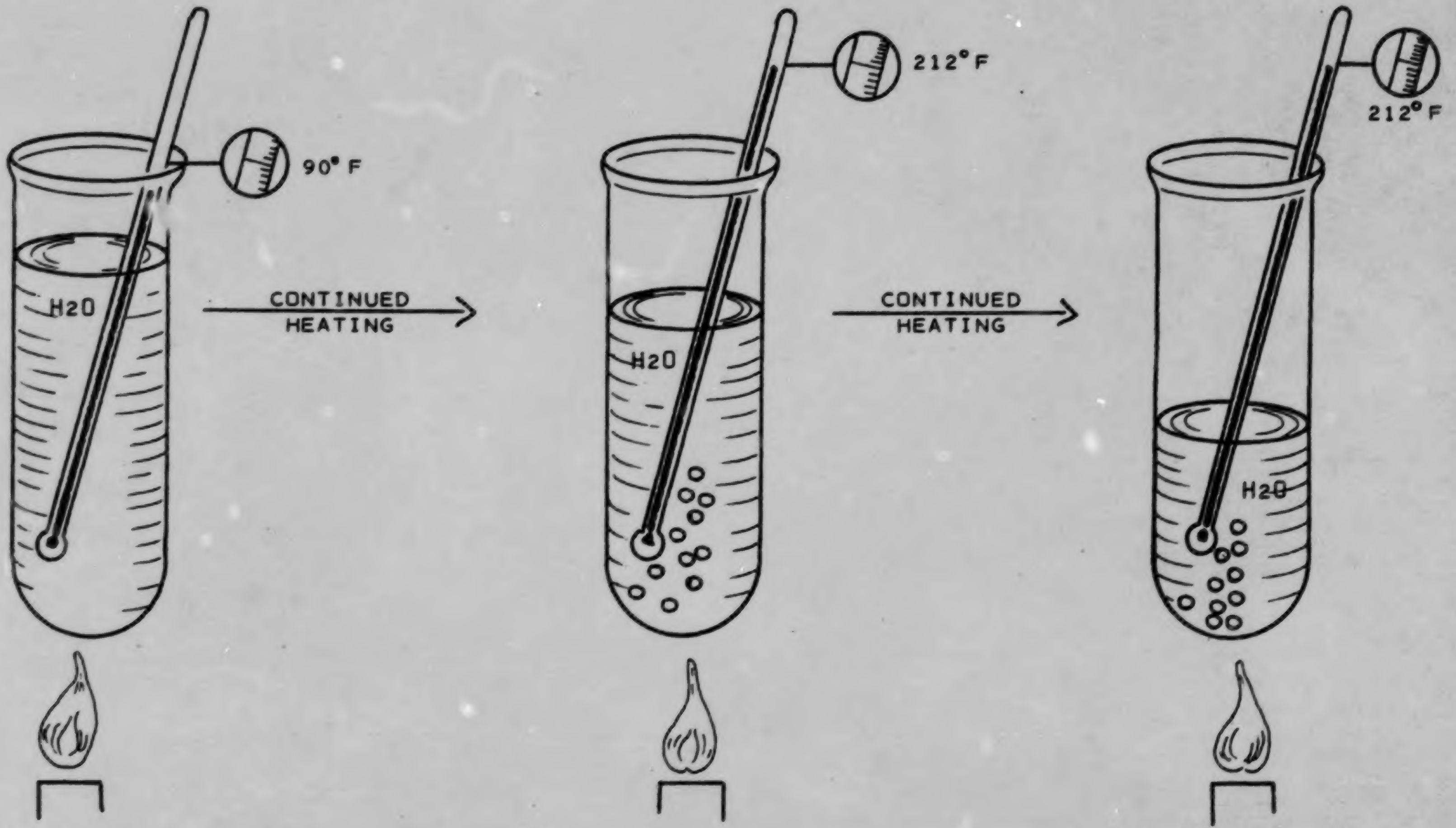
1 gallon of water = 8.34 pounds of water

$$8.34 \text{ lb} \times 972 \frac{\text{Btu}}{\text{lb}} = 8106 \text{ Btu}$$

Thus just to vaporize 150 gallons of water requires the absorption of approximately 8106 Btu of heat energy.

INITIALLY HEAT ENERGY INPUT CAUSES INCREASE IN TEMPERATURE.

LATER HEAT ENERGY INPUT CAUSES PHASE CHANGE TO OCCUR, AT CONSTANT TEMPERATURE AND PRESSURE.


90° F
H2O
CONTINUED HEATING
212° F
H2O
CONTINUED HEATING
212° F
H2O

AT A CONSTANT PRESSURE, TEMPERATURE OF PURE LIQUID RISES TO A SPECIFIC TEMPERATURE WHICH REMAINS UNTIL THE PHASE CHANGE (LIQUID → GAS) IS COMPLETE.

FIGURE 2

Question: How many Btu are required to raise the temperature of 150 gallons of water at 80°F to 212°F?

Answer: To solve this problem another term needs to be described - heat capacity (often called specific heat). Heat capacity can be described as the amount of heat required to raise the temperature of a specified mass of material a specified number of degrees. In the Metric System heat capacity has units of:

$$\frac{\text{calorie}}{\text{gram} \times \text{degree Celsius}} \quad \text{or} \quad \frac{\text{cal}}{\text{g.}^{\circ}\text{C}}$$

While in the "common" system the units are

$$\frac{\text{Btu}}{\text{pound x degree Fahrenheit}} \quad \text{or} \quad \frac{\text{Btu}}{\text{lb.}^{\circ}\text{F}}$$

For pure water the heat capacity (cp) is 1.00 $\frac{\text{cal}}{\text{g.}^{\circ}\text{C}}$ or 1.00 $\frac{\text{Btu}}{\text{lb.}^{\circ}\text{F}}$

To answer the question, then, the amount of heat required to raise 150 gallons of water from 80°F to 212°F is:

$$\text{heat} = 150 \text{ gal} \times \frac{1.00 \text{ Btu}}{\text{lb.}^{\circ}\text{F}} \times (212^{\circ}\text{F} - 80^{\circ}\text{F})$$

$$\text{heat} = 19800 \text{ Btu}$$

The heat capacity of ethanol 0.59 $\frac{\text{cal}}{\text{g.}^{\circ}\text{C}}$

or 0.59 $\frac{\text{Btu}}{\text{lb.}^{\circ}\text{F}}$ so that less heat is required to raise one gram of ethanol

one degree of temperature than an equal mass of water. Also a solution of ethanol/water will require more heat than pure ethanol but less heat than pure water to raise its temperature.

VI. Temperature

In the description of latent heat of fusion above, temperature was mentioned using two scales - Fahrenheit (°F) and Celsius (°C).

Note: Currently the United States of America is one of the few industrialized countries using the Fahrenheit scale for temperature instead of the Celsius scale.

On the Fahrenheit scale water (at one atmosphere of pressure) freezes at 32°F and boils at 212°F. This is a range of 180°F. On the Celsius scale water freezes at 0°C and boils at 100°C - a range of 100°C. SEE FIGURE 3.

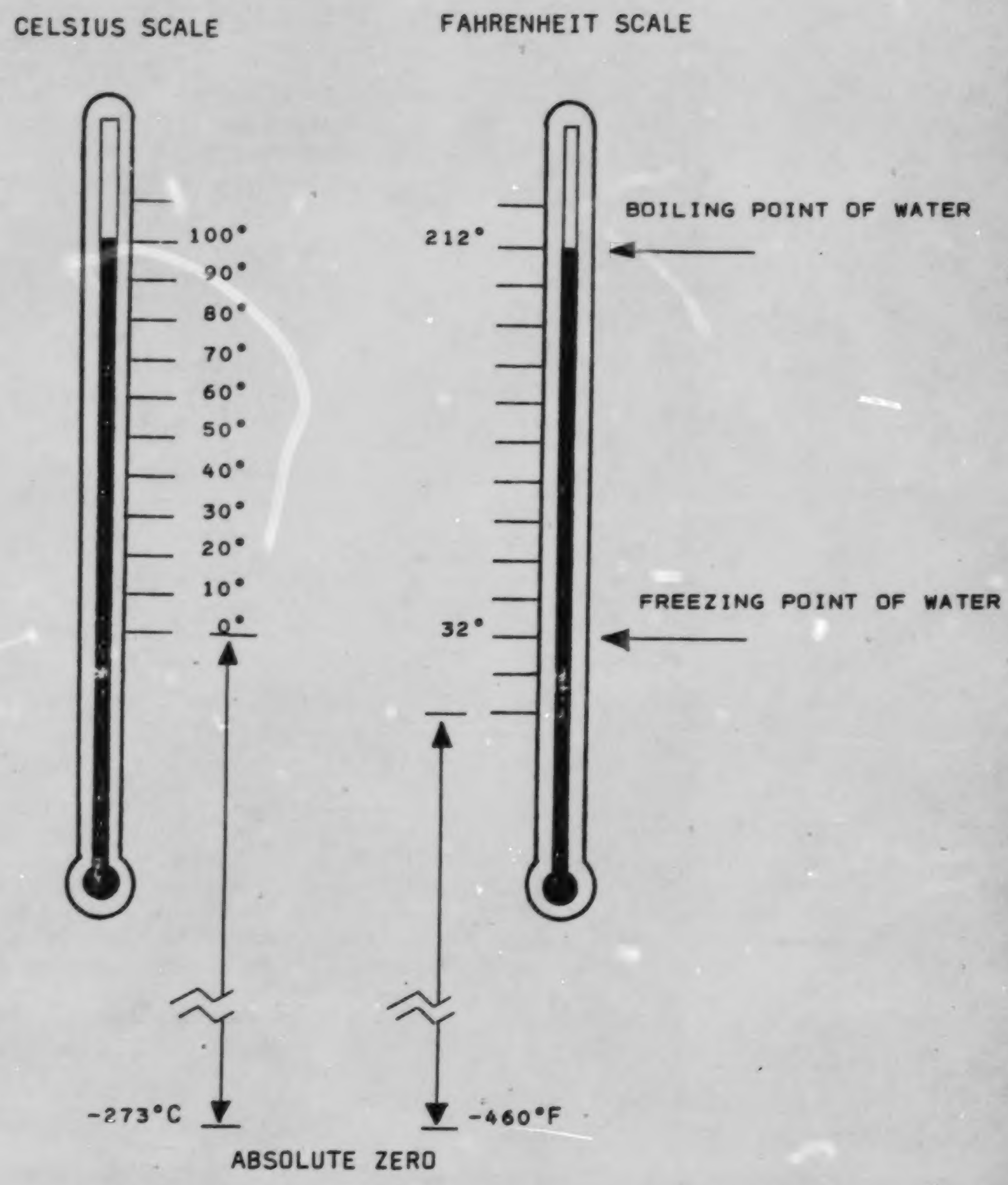

CELSIUS SCALE
FAHRENHEIT SCALE
100°
90°
80°
70°
60°
50°
40°
30°
20°
10°
0°
212°
BOILING POINT OF WATER
32°
FREEZING POINT OF WATER
-273°C
-460°F
ABSOLUTE ZERO

FIGURE 3

Therefore, a 180°F change in temperature is equivalent to a temperature change of 100°C. To convert a temperature reading in °F to one in °C:

$$^{\circ}C = \frac{5}{9} (^{\circ}F + 40) - 40$$

$$^{\circ}F = \frac{9}{5} (^{\circ}C + 40) - 40$$

Question: If a fermentation mixture is to be held at 88°F and your only thermometer reads in °C, what temperature reading in °C should you try to maintain for fermentation?

Answer: To convert from °F to °C use:

$$^{\circ}C = \frac{5}{9} (^{\circ}F + 40) - 40$$

$$^{\circ}C = \frac{5}{9} (88 = 40) - 40$$

$$^{\circ}C = \frac{5}{9} (128) - 40$$

$$^{\circ}C = 71.1 - 40$$

$$^{\circ}C = 31.1$$

Thus 31.1° is approximately equal to 88° F.

VII. Chemical Symbols

Each of the chemical elements has its own unique symbol made of one or two letters. For instance, hydrogen is symbolized by H; oxygen has the symbol O; carbon is C, and nitrogen is N.

A listing of more than one symbol next to each other represents a formula of a compound, i.e., a chemical made of more than one element. For example, C_2H_6O and CH_3CH_2OH (each of which shows two carbon atoms, six hydrogen atoms and one oxygen atom) are the formulas of ethanol - a product of alcoholic fermentation. The compound known as carbon dioxide has a chemical formula of CO_2; that is, one carbon atom linked to two oxygen atoms. You may already be aware that H_2O is a chemist's shorthand method for naming water. Glucose or dextrose, a sugar used by yeast to make ethanol has a chemical formula $C_6H_{12}O_6$.

VIII. Chemical Reactions and Equations

When one substance is converted into another substance, a chemical reaction occurs. The formation of substances from other substances is written in a shorthand fashion known as the chemical equation. For example: the combustion of ethanol in air (which contains oxygen gas) is written as:

$$CH_3CH_2OH + 3O_2 \rightarrow 2CO_2 + 3H_2O$$

Several points of interest should be noted. The formulas written to the left of the arrow are called reactants while those formulas on the right are products. This "balanced" chemical equation indicates that one CH_3CH_2OH molecule reacts with three O_2 molecules to yield two molecules of CO_2 and three molecules of H_2O. Note also that on the left side of the equation there is a total of two carbons, seven oxygens and six hydrogens. On the right side of the equation we find the same thing - 2-C, 7-O and 6-H. This exemplifies the concept that in chemical reactions matter (atoms) are neither created nor destroyed (just arranged). We started with two carbon atoms, for instance, and we ended up with two carbon atoms; not three; not one. In a chemical equation, new molecules are usually formed but not new atoms.

IX. Molecules and Atoms

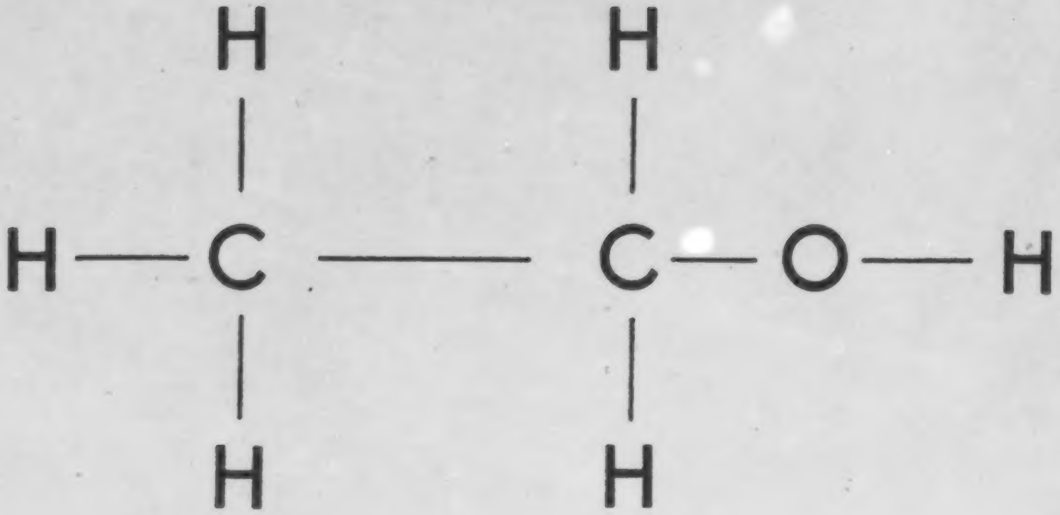
As written in the section on "MIXTURES and SOLUTIONS" the formula CH_3CH_2OH represents the compound called ethanol. This same formula is also used to describe a molecule of ethanol. A molecule of ethanol consists of two carbon atoms, six hydrogen atoms and one oxygen atom chemically bonded (linked) to each other in a particular fashion. SEE FIGURE 4.

These chemical bonds are usually quite strong. In fact, a solution of ethanol and water can be distilled by heating the liquid solution to a vapor and then condensing the vapor back to a liquid without destroying the chemical bonds of ethanol or of water.

The atoms which make up molecules are the smallest possible units of an element and are almost unchanged when they combine to form molecules. Molecules however can change quite significantly when they undergo chemical reactions.

X. Atomic Weights and Molecular Weights

When we speak of atomic weight we literally mean the mass of an atom but because weight is so firmly ingrained in chemistry literature the term atomic weight fluorishes. The lightest kind of atom is a hydrogen atom which has a weight of about 1.7×10^{-24} gram or 0.000000000000000-0000000017 gram. This small number is obviously unwieldy so chemists use a relative scale for describing atomic weight. The relative scale agreed upon is that the most common type of carbon atom has exactly 12 units of weight (mass). Using this relative scale of atomic weights hydrogen has an atomic weight of 1 unit; oxygen atoms are 16 units each; and nitrogen is 14 units.



$$\begin{array}{ccccccccc} & & H & & H & & & & \\ & & | & & | & & & & \\ H & - & C & - & C & - & O & - & H \\ & & | & & | & & & & \\ & & H & & H & & & & \end{array}$$

Ethanol: C_2H_6O, C_2H_5OH, CH_3CH_2OH, EtOH

Hydrogen atom = H

Carbon atom = C

Oxygen atom = O

Chemical bonds depicted by (-)

FIGURE 4

The molecular weight of a compound can be easily calculated by summing the appropriate atomic weights. For instance, glucose (dextrose) has a molecular formula of $C_6H_{12}O_6$. Its molecular weight is the sum of the atomic weights of six carbon atoms, twelve hydrogen atoms and six oxygen atoms.

$6 \times C = 6 \times 12 = 72$ units

$12 \times H = 12 \times 1 = 12$ units

$6 \times O = 6 \times 16 = \underline{96}$ units
180 units

A single molecule of glucose has a molecular weight of 180 units.

XI. Moles

Suppose you need to purchase 800 bolts from a hardware store. Instead of counting out exactly 800 bolts the clerk would probably determine how many pounds of bolts is equivalent to 800 bolts and then would weigh out that many pounds to sell to you. This approach would save both of you a lot of time and would result in your receiving if not exactly 800 bolts, approximately 800 of them. Chemists do virtually the same thing when they want a supply of molecules or atoms of a substance. In this case counting out individual atoms or molecules is not "inconvenient"; it is impossible!

If a chemist wanted 6.023×10^{23} atoms of carbon, he/she would weigh out 12 gram of carbon. If he/she wanted 6.023×10^{23} oxygen atoms, he/she would weigh out 16 gram of oxygen. Also, 6.023×10^{23} hydrogen atoms is equivalent to 1 gram of hydrogen. It is no coincidence that 6.023×10^{23} atoms of these (and any other) atoms weigh in grams the same value as their atomic weights. The system was planned that way. The number 6.023×10^{23} is known as a "mole", just as the number 144 is known as a "gross" and the number 12 is known as a "dozen". A mole of nitrogen atoms weighs 14 gram. A mole of glucose molecules weighs 180 gram (and is 6.023×10^{23} glucose molecules).

XII. Theoretical Yield

The concept of moles is based on relative atomic weights and can be useful in predicting the theoretical maximum quantity of products of a chemical reaction. This maximum quantity is known as the "theoretical yield" of a reaction.

Question: What is the theoretical yield of ethanol if 1 mole of glucose is used?

Answer: The balanced chemical equation showing glucose as a reactant and ethanol as a product is:

$$\underset{\text{glucose}}{C_6H_{12}O_6} \longrightarrow \underset{\text{ethanol}}{2CH_3CH_2OH} + 2CO_2$$

This is interpreted as one molecule of glucose yields two molecules of ethanol (and two molecules of carbon dioxide). Also, one mole of glucose yields two moles of ethanol. Thus, the theoretical yield (in moles) of ethanol is two moles. Note the theoretical yield of carbon dioxide is also two moles.

Question: What is the theoretical yield of ethanol (in grams) if 180 gram of glucose is used?

Answer: Because 180 gram of glucose is one mole of glucose we expect two moles of ethanol. But how many grams is this? One mole of ethanol is 46 gram (sum of atomic weights of CH_3CH_2OH expressed in grams). Two moles of ethanol is twice 46 grams or 92 grams. Thus, the theoretical yield (in grams) of ethanol is 92 grams. Note that the theoretical yield of carbon dioxide is 2 x 44 or 88 grams.

If, instead of 180 grams of glucose, 90 grams of glucose had been used (which is 90/180 or 1/2 mole of glucose) the theoretical yield of ethanol is one mole or 46 gram of ethanol. Also, the theoretical yield of carbon dioxide is 44 gram (one mole), if 90 grams of glucose is used.

XIII. Mixtures and Solutions

A mixture is a combination of two or more substances which may not be uniformly dispersed. The components of a mixture are not chemically combined to each other; they each retain their own set of physical and chemical properties and therefore can be separated from one another by appropriate means (filtration, freezing, distillation, etc.) A true solution is a mixture which is uniformly dispersed at the molecular level. All solutions are mixtures but not all mixtures are solutions. Alcohol dissolved in water is a mixture called a solution. Sand mixed with sugar is a mixture but not a solution.

XIV. Volume, Density and Specific Gravity

In the section entitled Moles it has been noted that to measure specific numbers of atoms or molecules, one needs only to weigh out the proper mass of the substance. One mole (6.023×10^{23} atoms) of carbon is obtained by weighing out 12 grams of pure, solid carbon. This procedure works for liquids as well...one mole of ethanol is 46 grams of ethanol. A corresponding volume of ethanol could be measured out in a calibrated container. This procedure is frequently used to isolate a specified quantity of a liquid.

Volume can be measured in the common units of fluid ounces, pints, quarts, gallons or in metric units such as milliliters (cubic centimeters) or liters.

Metric Units	Common (English) Equivalent
Liter (ℓ)	1.06 quarts (qt)
Milliliter (mℓ) = 0.001 ℓ	0.0340 fluid ounces (oz)

A cubic centimeter (cm or cc) is just what the name implies - a cube, one centimeter on a side. SEE FIGURE 5.

This is also called milliliter (mℓ). A liter (ℓ) is one thousand milliliters and is the volume of a cube which is 10 centimeters on a side.

The term density is a ratio of mass divided by volume. Common units of density are $\frac{\text{pounds}}{\text{cubic ft.}}$ and $\frac{\text{grams}}{\text{cubic centimeter}}$

$\frac{\text{lb}}{\text{A3}}$ and $\frac{\text{g}}{\text{cm}^3}$ i.e., $\frac{\text{g}}{\text{cc}}$

Water at room temperature has a density of about 62.4 lb/ft^3 or 0.79 g/cm^3. Thus water is more dense than ethanol and it is frequently said that water is "heavier" than ethanol though, strictly speaking, the use of "heavier" here is incorrect. SEE FIGURE 6.

In the laboratory a common device for measuring volume is a graduated cylinder. SEE FIGURE 7a.

Usually, graduated cylinders are graduated in units of milliliters (cubic centimeters). Suppose you had no balance on which to weigh out 46 grams of ethanol but you knew the density of ethanol at room temperature is 0.79 g/cm^3.

$$46 \text{ grams} \times \frac{1 \text{ cm}^3}{0.79 \text{ g}} = 36.34 \text{ cm}^3 = 36.34 \text{ ml}$$

Thus by measuring a volume of 36.34 ml of ethanol into the graduated cylinder, you would have 46 grams of ethanol without actually weighing it on a balance. It should be noted that water and ethanol and mixtures of these have a "concave" meniscus. That is the surface of the liquid in a container like a graduated cylinder has a curvature similar to that shown in FIGURE 7b.

When volume readings are made with a graduated cylinder of liquids with a concave meniscus, it is the lowest point of the meniscus which is used to read the volume of the liquid. In FIGURE 7b the correct volume is 36.34 ml, not 36.60 ml.

The term specific gravity is the density of a substance divided by the density of water. The specific gravity of ethanol is:

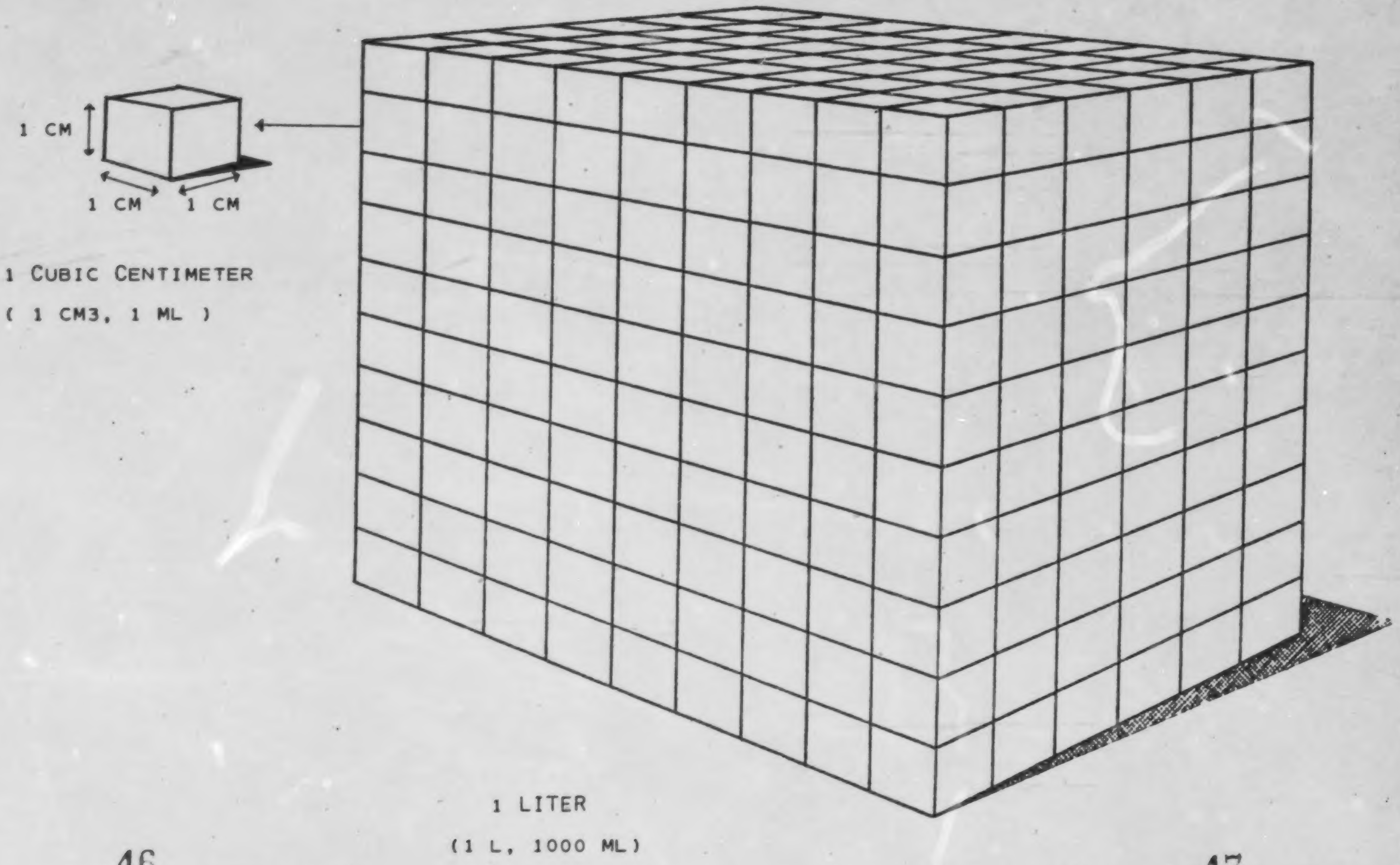
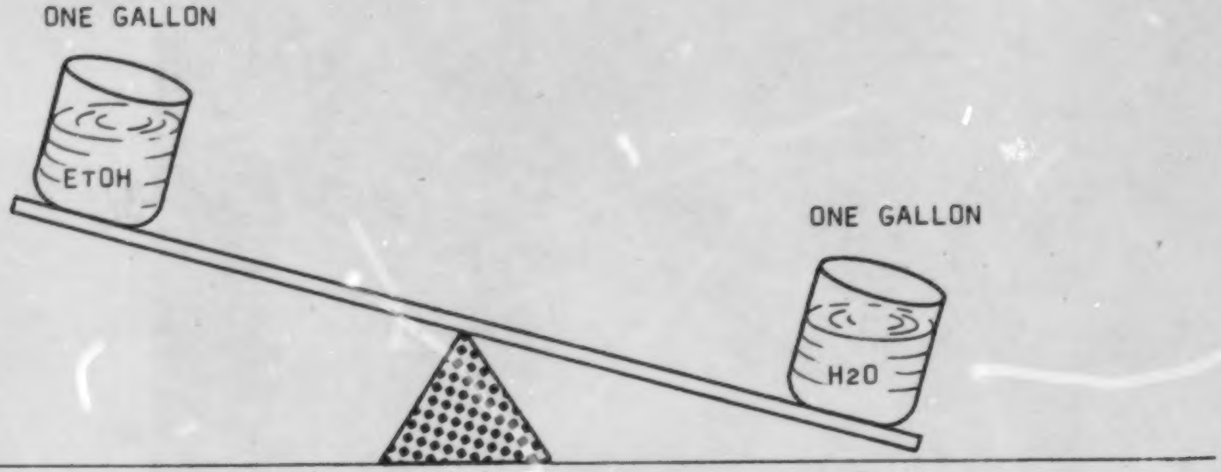
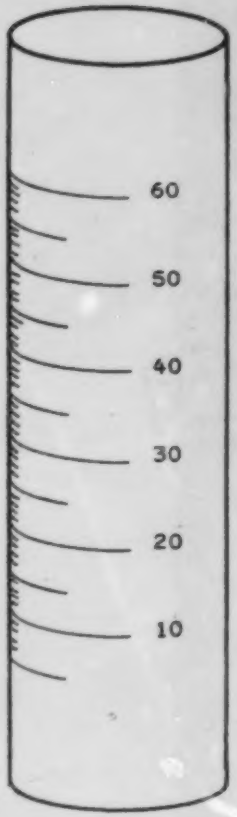

1 CM
1 CM
1 CM
1 CUBIC CENTIMETER
(1 CM3, 1 ML)
1 LITER
(1 L, 1000 ML)

FIGURE 5

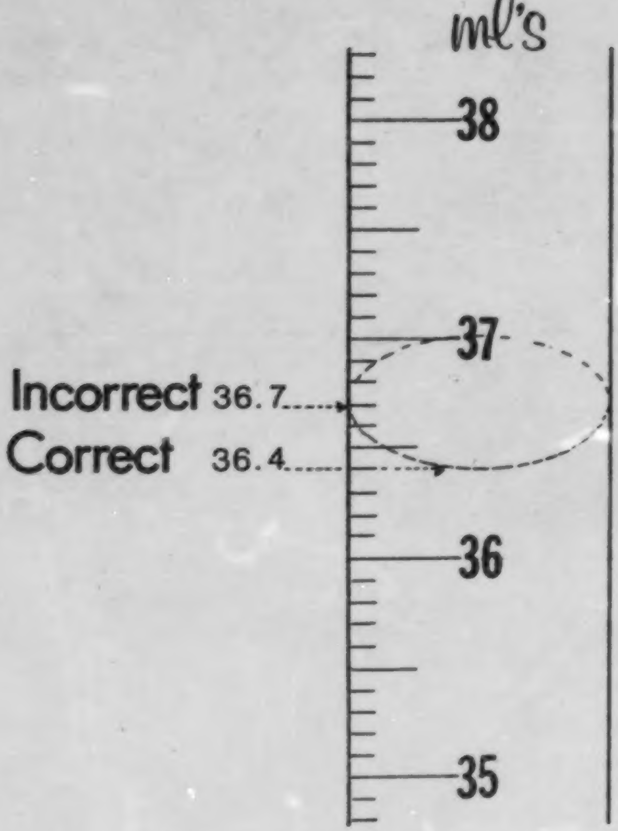

ONE GALLON
ETOH
ONE GALLON
H2O

ETHANOL IS LESS DENSE THAN WATER, I.E. ETHANOL HAS LESS MASS PER UNIT OF VOLUME.

FIGURE 6

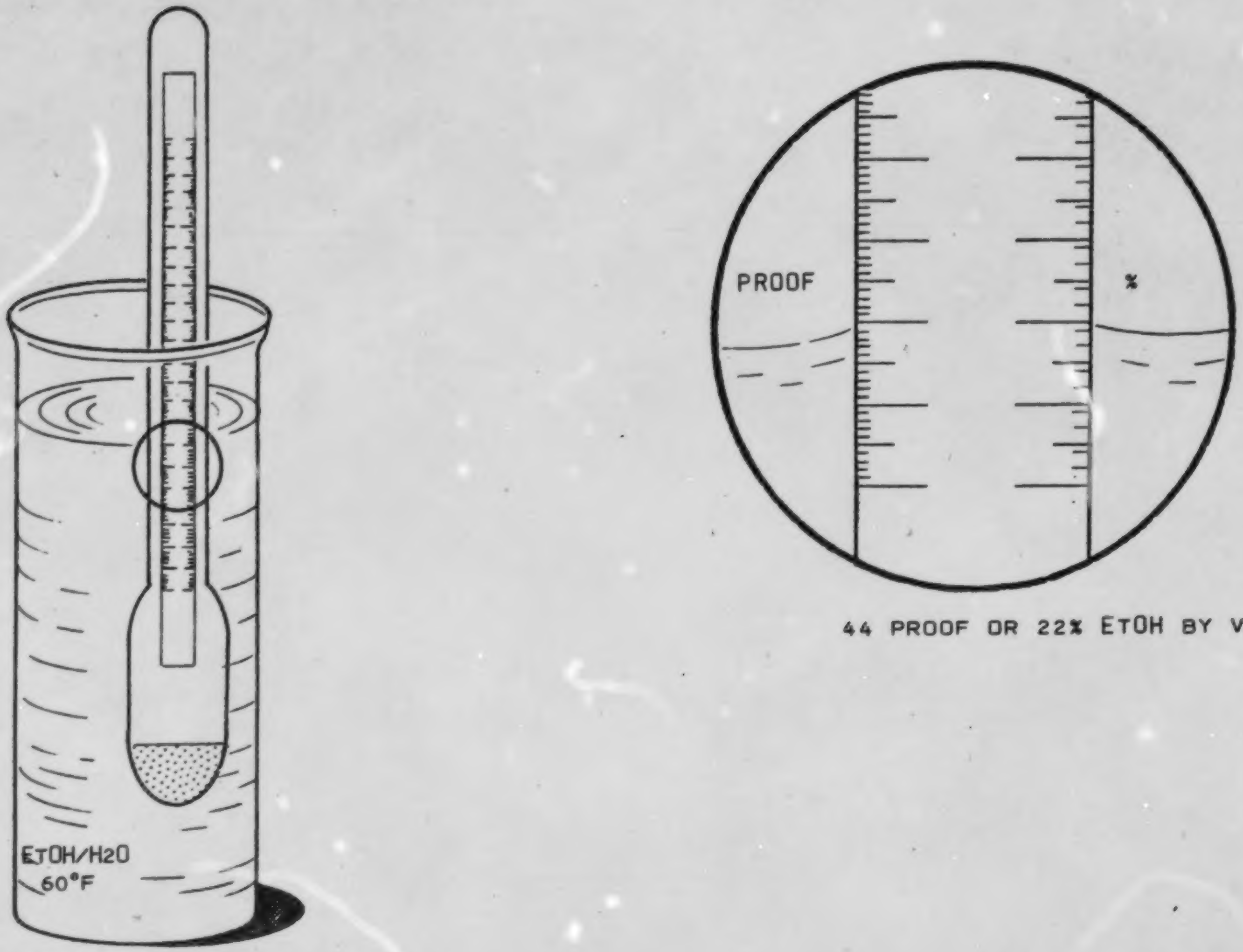

60
50
40
30
20
10

GRADUATED CYLINDER


ml's
38
37
Incorrect 36.7
Correct 36.4
36
35

THE MENISCUS BOTTOM INDICATES THE VOLUME READING, NOT THE TOP.

FIGURE 7a


PROOF
%
ETOH/H2O
60°F

HYDROMETER

44 PROOF OR 22% ETOH BY VOLUME

FIGURE 7b

$$\frac{\text{density of ethanol}}{\text{density of water}}$$ - using metric terms this calculation is:

$$\frac{0.79\ g/cm^3}{1.00\ g/cm^3} = 0.79$$

Note that specific gravity has no "dimensions" or "units" like grams and cubic centimeters. The specific gravity of ethanol as determined with densities of lb/ft^3 is also 0.79.

Specific gravity is the basis by which the concentration of ethanol distillate is commonly measured. A hydrometer floats in the ethanol/water solution as shown in FIGURE 8a. The level at which the hydrometer floats in the solution is a measure of the specific gravity of the solution which in turn is a measure of the proof or concentration of ethanol in water. The lower the hydrometer sinks into the solution, the lower the specific gravity of the solution is and the greater the concentration of ethanol is.

Hydrometers used to measure the concentration are usually calibrated in units of proof and percent by volume. SEE FIGURE 8b. "Proof" is simply the ethanol content of solution at 60°F stated as twice the percent of ethanol by volume. If a hydrometer is used in a solution at a temperature different than 60°F, a correction must be made to obtain the true proof or true percent ethanol by volume. APPENDIX A is used to convert apparent proof readings at temperatures other than 60°F to "true" proof readings at 60°F.

XV. Acids and Bases

A. Concept of Acids and Bases

The amount of acid or base present in a fermenting solution affects the performance of the yeast and so affects the production of ethanol. A knowledge of the nature of acids and bases is therefore important for the ethanol plant operator.

Although there are more than one definition of acid, we shall define acid as a substance which when dissolved in water, produces H^+ ions in water. An H^+ ion is known as a "hydrogen ion" or a "proton". A base can be defined as a substance which, when dissolved in water, produces OH^- ions, i.e. hydroxide ions.

An example of an acid used in ethanol production is sulfuric acid. The sulfuric acid molecule is H_2SO_4 and is an acid because of the action described by the following balanced chemical equation:

$$H_2SO_4 \longrightarrow H^+ + HSO_4^-$$

Note that the H_2SO_4 molecule breaks up into an H^+ ion and an HSO_4^- ion. Because H_2SO_4 produces H^+ ion the compound is called an acid.

A base commonly used in adjusting acidity/basicity in mash is calcium hydroxide also known as calcium hydrate, hydrated lime, caustic lime and slaked lime. When dissolved in water calcium hydroxide produces hydroxide ions and is therefore a base.

$$Ca(OH)_2 \longrightarrow Ca^{2+} + 2\ OH^-$$

B. Acid - Base Neutralization

Acids react with bases to neutralize each other according to the following equation:

$$H^+ + OH^- \longrightarrow H_2O$$

If equal numbers of moles of H^+ and OH^- ions are combined neutral water H_2O is formed and the solution is said to be "neutral". If the solution contains more H^+ ions than OH^- ions, the solution is said to be acidic. Conversely, a water solution (aqueous solution) which has more OH^- ions than H^+ ions is basic.

If a mash is too acidic, calcium hydroxide can be added to consume the excess H^+ ions. If a mash solution is too basic (less likely than the first situation) sulfuric acid can be added to increase the H^+ concentration (decrease the OH^- concentration).

Concentrated acids and bases should not be mixed together since considerable quantities of heat are liberated by the neutralization reaction. The reaction mixture could literally boil, spewing acids or bases into the air.

C. Units of Acidity; pH

The acidity of a mixture is most often described in terms of pH. The term "pH" is becoming more familiar to the public with advertisements stating "our shampoo is pH - balanced" and the like. (pH is a shorthand method of reporting acidity and basicity.)

Typically the scale of pH is from 1 to 14 with 7.00 being the pH of a "neutral" solution; lower values of pH are acidic; higher pH values are basic. SEE FIGURE 8.

Mathematically, $pH = {}^-\log_{10} [H^+]$ which is more or less in plain English, pH equals minus the logarithm, base 10, of the hydrogen ion molarity. Molarity is a way of describing concentration and is defined as "the number of moles per liter of solution". Here we are concerned with the number of moles of H^+ per liter of solution i.e. $[H^+]$. The word "logarithm; base 10" means the exponent or power of 10 which equals the molarity of H^+, in this instance. For example, if the molarity of H^+ is 1.00×10^{-7} then:

$[H^+] = 1.00 \times 10^{-7}$

$pH = {}^{-}\log_{10} [H^+]$

$pH = {}^{-}\log_{10} (1.00 \times 10^{-7})$

$pH = {}^{-}(0.00 - 7.00)$

$pH = 7.00$

A solution which has a hydrogen ion molarity of 1.00×10^{-5} would have a pH of 5 since

$pH = \log_{10} [H^+]$

$pH = {}^{-}\log_{10} (1.00 \times 10^{-5})$

$pH = -(0.00 - 5.00)$

$pH = 5.00$

This solution, having a pH less than 7.00, is acidic. The higher the concentration of H^+ is, the lower the pH is and the more acidic the solution is. Each pH unit represents a 10-fold change in H^+ ion concentration.

The concentration (molarity) of H^+ ions in a mash solution can be determined if the pH is known (see Sections I, L 4, 5). For example, say you determine that a mash solution has a pH of 4.3 and you wish to calculate the molarity of H^+ ion.

$pH = {}^{-}\log_{10}[H^+] = 4.3$

$\log_{10}[H^+] = -4.3$

But -4.3 is 0.7 -5 so,

$\log_{10}[H^+] = 0.7 - 5$

$[H^+] = \text{antilog } (0.7-5) = \text{antilog } (0.7) + \text{antilog } (-5)$

$[H^+] = 5.0 \times 10^{-5}$

Thus a pH of 4.3 corresponds to a hydrogen ion of 5.0×10^{-5} moles per liter.

Aqueous (water solutions always have both H^+ ions and OH^- ions present and at 25°C the product of the molarities of these ions is 1×10^{-14}.

$[H^+] \times [OH^-] = 1 \times 10^{-14}$

If the $[H^+]$ is known then the $[OH^-]$ can be calculated as follows:

Let $[H^+] = 5.0 \times 10^{-5}$ moles per liter

$$[OH^-] = \frac{1 \times 10^{-14}}{[H^+]}$$

$$[OH^-] = \frac{1 \times 10^{-14}}{5.0 \times 10^{-5}}$$

$$[OH^-] = 2 \times 10^{-8}$$

Similarly, if a basic solution has a known concentration of OH^- ions, the H^+ concentration can be calculated and then the pH. For example: What is the pH of a 0.01 molar OH^- solution?

$$[OH^-] = 0.01 = 1 \times 10^{-2}$$

$$[H^+] = \frac{1 \times 10^{-14}}{[OH^-]} = \frac{1 \times 10^{-14}}{1 \times 10^{-2}}$$

$$[H^+] = 1 \times 10^{-12}$$

$$pH = {}^-\log_{10}[H^+]$$

$$pH = {}^-\log_{10}(1 \times 10^{-12})$$

pH = 12, which is certainly basic, being a value greater than 7.00.

D. Acid - Base Indicators

Acid-Base indicators are chemical dyes that change color at a certain pH value. The dye is exposed to the solution to be tested and then the color of the dye is determined. The color correlates to concentration of H^+ and therefore to the pH of the test solution. One of the first dyes to be used is litmus. Litmus can be impregnated onto a strip of absorbent paper that gives us "litmus paper" which is commonly used in chemistry laboratories and sometimes in alcohol production work. Litmus turns red in acid and blue in base but is not sensitive enough to pinpoint the pH of a solution.

Another type of colorimetric determination of acid-base is pH paper, which is reasonably effective at indicating pH. On such paper is impregnated a mixture of dyes (indicators) which change color over a wide range of pH values.

When a strip of pH paper is dipped into a test solution, the resulting color of the paper (actually the dyes in the paper) is compared to a color chart provided with the pH paper. By matching the color of the paper with the color chart, the pH of the solution can be approximated.

E. pH Meters

A pH meter is an electronic device which measures pH. A direct reading meter displays a numerical value of pH either by movement of a needle across the face of a scale or by digital readout.

To measure the pH of a mash for instance, the pH meter must be calibrated first. This is accomplished by immersing the pH electrode into a reference solution of known pH. The meter is then adjusted to read-out that particular pH value. Next the electrode is removed from the reference solution, rinsed with distilled water and immersed into the mash. After a few (2-10) seconds the pH of the mash is read directly from the meter.

pH meters cost more than pH paper and are less convenient but more accurate. At the time of writing, pH meter prices varied from $110 to several hundred dollars.

XVI. Summary:

This module of Chemistry is not meant to be the sole source of chemistry information to the student. It is hoped that the student has available a number of chemistry source books like those listed under References for this module.

pH OF SOME COMMON SOLUTIONS

Battery Acid	0	
Stomach Acid	1.4 - 1.8	
Lemon Juice	2.1	
Vinegar	2.9	
Soda Water	3.0	
Wine	3.5	
Tomato Juice	4.0	
Coffee	5.0	
Urine, Sour Milk	6.0	
Rainwater	6.5	
Pure Water, 25°C	7.00	NEUTRAL
Blood	7.35 - 7.45	
Seawater	8.0	
Soaps, Shampoos	8.0 - 9.0	
Detergents	9.0 - 10.0	
Milk of Magnesia	10.0	
Household Amonia	11.9	
Liquid Bleach	12.0	
Household Lye	14.0	

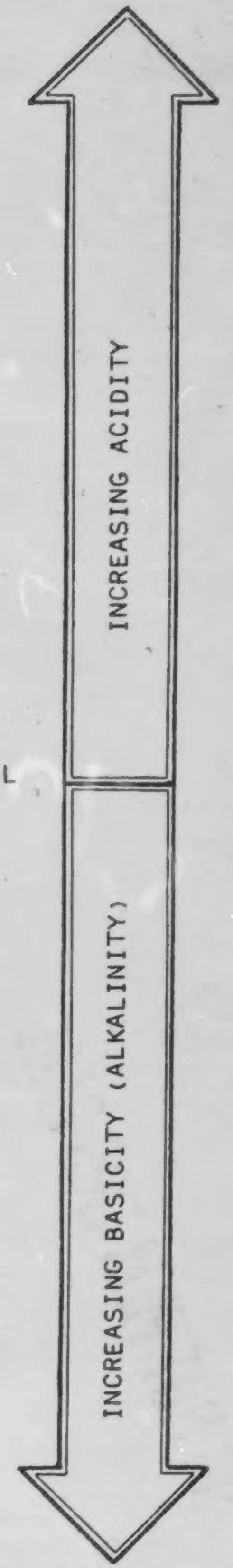

INCREASING ACIDITY
INCREASING BASICITY (ALKALINITY)

FIGURE 8

ALCOHOL FUEL PRODUCTION

MODULE III - MICROBIOLOGY

I. Introduction:

A general knowledge of enzymes, their physical and chemical properties, nutritional needs, and mechanism of action is necessary for the successful production of alcohol. In addition, specific enzymes have optimum and specific conditions for efficient reaction, and contamination control is necessary for quality output. An understanding of basic microbiology provides the "why" for quality control.

In this module, the process of making alcohol is discussed in general, and this is followed by specific enzyme information.

II. Objectives:

Upon completion of this module, the student will be able to:

A. Identify terms and definitions related to the microbiology involvement of alcohol fuel production.

B. Point out the basic chemical processes involved in making ethanol.

C. Outline the procedure for making alcohol from grain.

D. Outline the procedure for making alcohol from sugar.

E. List the three basic classes of carbohydrates.

F. Point out how fermentation occurs through use of enzymes, glucose and yeasts, and explain the methods and importance of sterilization.

III. Instructional Materials:

A. Agar Plates

B. Wire Loops

C. Glassware - Beakers, jars, graduated cylinders, stirring rods

D. Agar solution

E. Laboratory oven

F. Bunsen Burners

G. Matches

H. Thermometers

I. Yeast, enzymes, antibioties, etc.

J. Timers, hotplates, and parafilm

IV. References:

A. Elements of General and Biological Chemistry. Ed. John R. Holum. 2nd Ed., New York: John Wiley & Sons, Inc. 1962.

B. Fuel From Farms. "A Guide to Small Scale Ethanol Production." Solar Energy Research Institute. SERI 451 519 UC-61. May 1980.

C. "High Fructose Corn Syrup at 4 Million Pounds/Day." Food Engineering. Ed. James R. Russo. 61/Int-37. May 1976.

D. The Manufacture of Products From Corn. 10th Edition. 1976.

E. Noller, Carl R., Chemistry of Organic Compounds. 2nd Edition. Philadelphia: W. B. Saunders Company, 1958.

F. Technical Methods of Analysis as Employed in the Laboratories of Arthur D. Little, Inc., Cambridge, Mass., 1st Edition. New York: McGraw Hill Book Company, Inc. 1921.

MODULE III - MICROBIOLOGY

OUTLINE

- I. The Chemical Process
  - A. Acid Hydrolysis
  - B. Enzymatic
  - C. Carbohydrates
    - 1. General
    - 2. Hexose
    - 3. Glucose
    - 4. Fructose
    - 5. Starch
    - 6. Cellulose
  - D. Stochiometry
- II. Alcohol from Grain
- III. Alcohol from Sugar
- IV. Carbohydrates and Fermentables
  - A. Monosaccharides
  - B. Dicharrides
  - C. Polysaccharides
- V. Basic Microbiology
  - A. Enzymes
  - B. Pathways
  - C. Yeasts
    - 1. Types
    - 2. Propogation
    - 3. Life Cycle
  - D. Antibiotics
  - E. Water Activity

MODULE III - MICROBIOLOGY

Terms and Definitions:

1. Catalyst - a substance (as an enzyme) that initiates a chemical reaction and enables it to proceed under milder conditions (as at a lower temperature) than otherwise possible.

2. Enzymes - Substances that are produced by living cells and bring about or accelerate reactions at body temperature without themselves undergoing marked destruction in the process.

3. Azeotrope - A liquid mixture which exhibits a maximum or a minimum boiling point relative to the boiling points of surrounding mixture compositions.

4. Substrate - The base on which an organism lives.

5. Wort - The liquid remaining from brewing mash preparation following the filtering step or alutering or fermentable beer.

6. Procaryote - A cellular organism that does not have a distinct nucleus.

7. Eurcaryote - An organism composed of one or more cells with visibly evident nuclei.

8. Solute - A dissolved substance.

9. Fermentation - An enzymatically controlled anaerobic breakdown of an energy rich compound (as a carbohydrate to carbon dioxide and alcohol).

10. Distillation - A process that consists of driving gas or vapor from liquids or solids by heating and condensing to liquid products and that is used especially for purification, fractionation, or the formation of new substances.

11. Sucrose - A sweet crystalline dextrorotatory non-reducing disaccharide sugar $C_{12}H_{22}O_{11}$ that occurs naturally in most land plants and is the sugar obtained from sugarcane and sugar beets.

12. Glucose - A sugar $C_6H_{12}O_6$ known in dextrorotatory, levorotatory, and racemic forms.

13. Levulose - Fructose 2.

14. Amylose - Any of various polysaccharides as starch or cellulose.

15. Amylopectin - A component of starch that has a high molecular weight and branched structure and does not tend to gel in aqueous solutions.

16. Maltase - An enzyme that accelerates the hydrolysis of maltose to glucose.

17. Maltose - A crystalline dextrorotatory fermentable sugar $C_{12}H_{22}O_{11}$ formed from starch by amylose.

18. Reflux - to heat so that the vapors formed condense and return to be heated again.

19. Hexose - A monosaccharide (as glucose) containing six carbon atoms in the molecule.

20. Hydrolyzed - to undergo hydrolysis.

21. Hydrolysis - A chemical process of decomposition involving splitting of a bond and addition of the elements of water.

ALCOHOL FUEL PRODUCTION

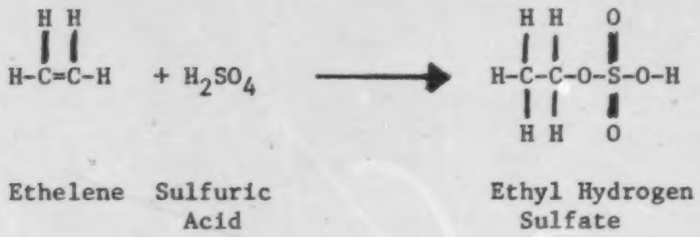
MODULE III - MICROBIOLOGY

I. The Chemical Process:

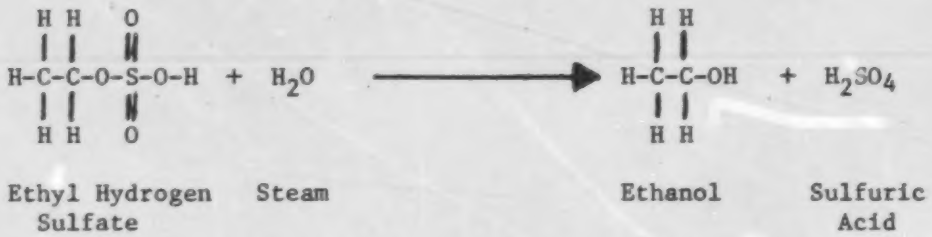
Ethyl alcohol (ethanol) the most promising answer to the liquid fuels movement from renewable materials, can be made from many carbohydrates. An introduction to the basic chemistry of ethanol shows the possibilities.

A. Acid Hydrolysis

Ethyl alcohol can be produced from ethelene (a petroleum product), by acid hydrolysis which is the method now used most often.



$$\mathrm{H{-}\overset{H}{C}{=}\overset{H}{C}{-}H} + H_2SO_4 \longrightarrow \mathrm{H{-}\underset{H}{\overset{H}{C}}{-}\underset{H}{\overset{H}{C}}{-}O{-}\underset{O}{\overset{O}{S}}{-}O{-}H}$$



$$\mathrm{H{-}\underset{H}{\overset{H}{C}}{-}\underset{H}{\overset{H}{C}}{-}O{-}\underset{O}{\overset{O}{S}}{-}O{-}H} + H_2O \longrightarrow \mathrm{H{-}\underset{H}{\overset{H}{C}}{-}\underset{H}{\overset{H}{C}}{-}OH} + H_2SO_4$$

This method would do nothing to relieve the problem of petroleum supplies, but as the major source governs the price of ethanol.

B. Enzymatic

Ethyl Alcohol can also be produced from the enzymatic fermentation of carbohydrates.

$$C_6H_{12}O_6 \xrightarrow[\text{ENZYMES}]{\text{ZYMASE}} 2C_2H_5OH + 2CO_2$$

Hexose   Ethanol   Carbon Dioxide

This method uses renewable sources.

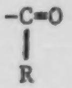
Zymase is the name of an enzyme group found in yeast.

Enzymes are catalysts which cause a set of complex reactions to occur faster than without the catalysts. The enzymes eventually emerge unchanged so that they can be used over and over.

C. Carbohydrates

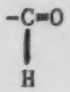
The simple sugars (Hexoses) come from carbohydrates.

1. Carbohydrates are compounds containing carbon, hydrogen, and oxygen. They are polyhydroxyl (contain many OH groups) and contain either the aldehyde or ketone structural groups:



$$\begin{array}{c}-C=O\\ |\\ R\end{array}$$

Aldehyde



$$\begin{array}{c}-C=O\\ |\\ H\end{array}$$

Ketone

Carbohydrates may be monosaccharides (simple sugars), oligosaccharides (polymlrs of 2-10 molecules of monosaccharides) or polysaccharides (polymlrs of 11 or more molecules of monosaccharides).

All have the -OSE name ending.

2. Hexose is a simple sugar (Monosaccharide) containing six carbon atoms.

Glucose - $C_6H_{12}O_6$
Fructose - $C_6H_{12}O_6$
Mannose - $C_6H_{12}O_6$
Galactose - $C_6H_{12}O_6$

ALL HAVE
THE SAME
CHEMICAL
FORMULA,
BUT MGT
THE SAME
STRUCTURAL
FORMULA

Two of these simple sugars, glucose and fructose, are the building blocks for most carbohydrates.

These two hexoses (6-carbon sugars) diagrammed below in linear and ring form, are the major components of such things as sucrose (table sugar), corn, wheat, other grains, sorghum, sugar beets, potatoes, fruits, and even wood (cellulose), all of which can be sources of ethanol.

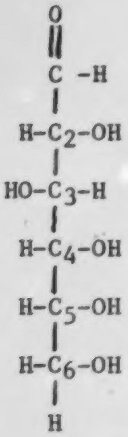
3. Glucose (Dextrose):

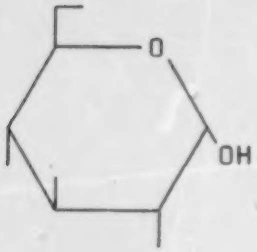
LINEAR

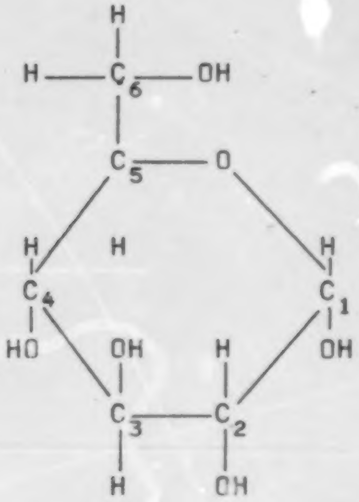
CONDENSED SYMBOL

* RING

THE OXYGEN ON CARBON 1 CAN LINK WITH CARBON - 5 TO FORM A RING COMPOUND


O
C -H
H-C2-OH
HO-C3-H
H-C4-OH
H-C5-OH
H-C6-OH
H



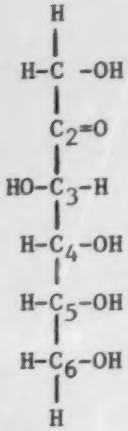

H
H
C6
OH
C5
O
H
H
H
C4
C1
HO
OH
H
OH
C3
C2
H
OH

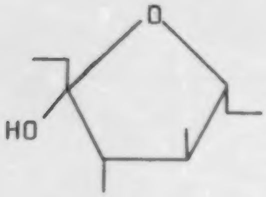
4. Fructose (Levulose):

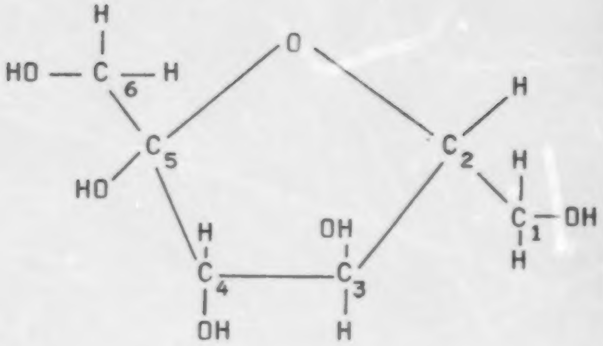
LINEAR

CONDENSED SYMBOL

* RING

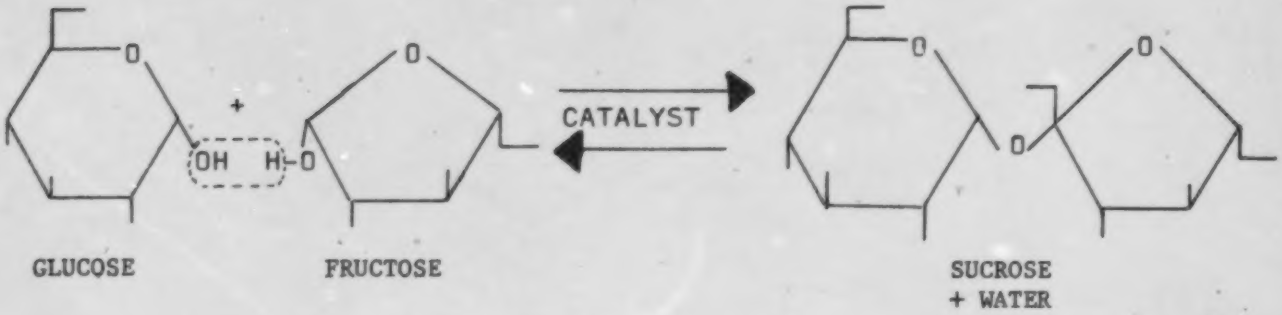

H
H-C -OH
C2=O
HO-C3-H
H-C4-OH
H-C5-OH
H-C6-OH
H




H
HO
C6
H
O
H
C5
C2
HO
H
H
OH
C1
OH
C4
C3
H
OH
H

*There are other possible ring structures.

The sucrose (table sugar) molecule is composed of 1 glucose molecule and 1 fructose molecule less 1 water molecule:



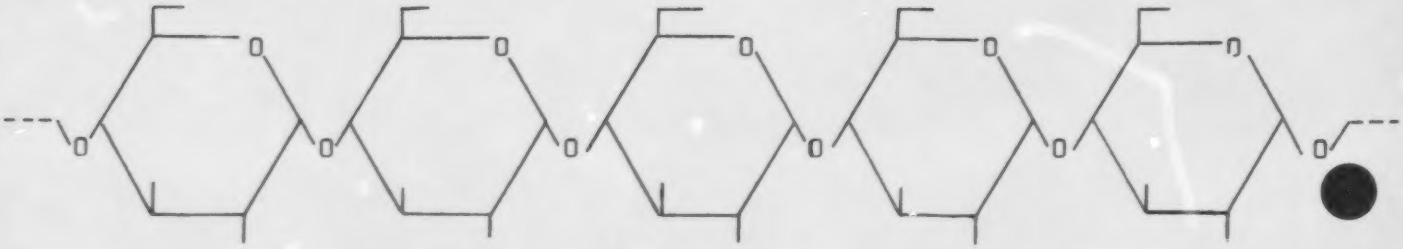
Upon Hydrolysis (addition of water) the reverse reaction occurs:

$C_{12}H_{22}O_{11}$ + H_2O $\xrightarrow[\text{INVERTASE}]{\text{ENZYME}}$ $2C_6H_{12}O_6$

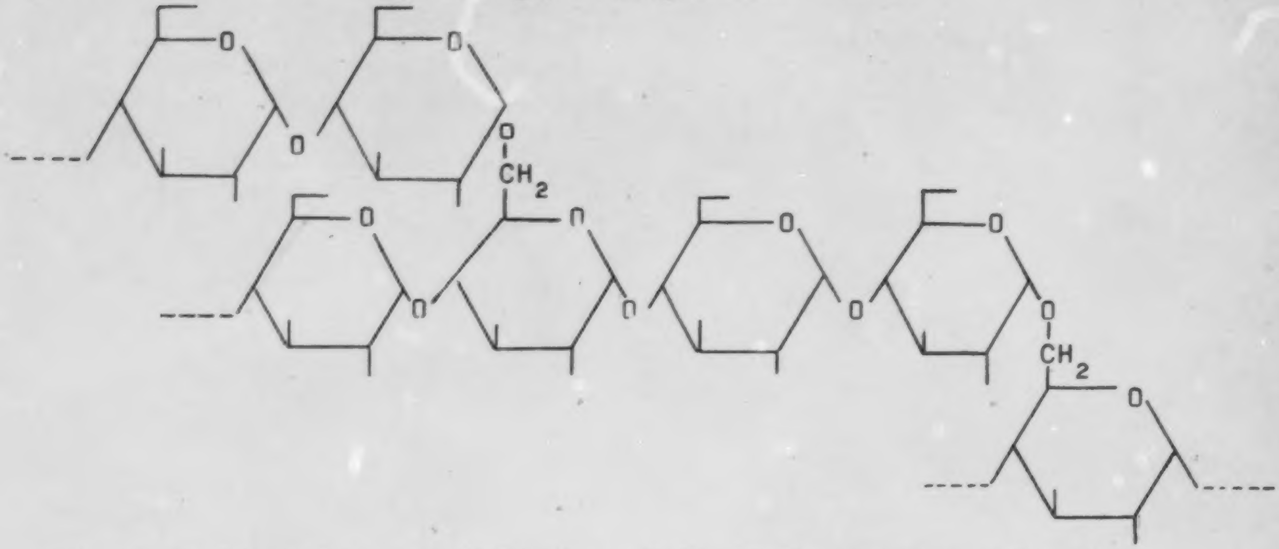
SUCROSE WATER 1 GLUCOSE
1 FRUCTOSE

5. The starch molecule is a means of storing energy by corn and other plants. It consists of chains (polymers) of glucose molecules less 1 water molecule at each junction. Starch forms two different (structural) forms of polymers:

a. Amylose - Chains of glucose molecules joined to each other at the 1 and 4 carbons (1-4 linkage) forming straight chains:



b. Amylopectin - Chains of glucose molecules joined at the 1-6 carbons (1-6 Linkage) forming branched chains:



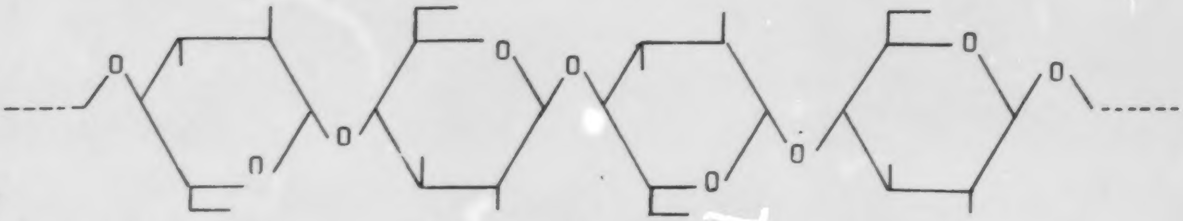
The starch molecule is more difficult to "unlock" than sucrose, and must be carefully "cooked" with enzymes, then treated with other enzymes to form fermentable hexoses:

$$\text{STARCH 1-4 LINKAGE} + \text{HOH} \xrightarrow[\text{ENZYME}]{\alpha\ \text{AMYLASE}} \text{MALTOSE}$$

$$\text{STARCH 1-6 LINKAGE} + H_2O \xrightarrow[\text{ENZYME}]{\beta\ \text{AMYLASE}} \text{MALTOSE}$$

$$\text{MALTOSE} + H_2O \xrightarrow[\text{ENZYME}]{\text{MALTASE}} \text{GLUCOSE}$$

6. Cellulose (wood, paper, etc.) conversion to ethanol is an interesting area which is receiving much attention at this time. This complicated glucose polymer requires special enzymes (possible obtained from termites) to release the hexose.



Note that every other glucose unit is inverted. Enzymes are sensitive to molecular orientation.

D. Stochiometry

Cellulose is a linear polymer of glucose but of -D-Glucose rather than -D-Glucose as seen in sucrose and starch. Cellulose molecules have much longer chains (thousands of molecules in length) and are insoluble in water and all organic solvents. Complete hydrolysis has been extremely difficult and costly to date.

Once hexoses have been formed the fermentation to ethanol is the same:

$$\underset{\text{Hexose}}{C_6H_{12}O_6} \xrightarrow[\text{Enzymes in Yeast}]{\text{Zymase}} \underset{\text{Ethanol}}{2C_2H_5OH} + \underset{\text{Carbon Dioxide}}{2CO_2}$$

And by using molecular weights calculations can be made on yields from various raw materials.

$$\underset{180}{C_6H_{12}O_6} \longrightarrow \underset{92}{2C_2H_5OH} + \underset{38}{2CO_2}$$

This means that 180 pounds of total sugar (or carbohydrate) content yields approximately 92 pounds of ethanol. NOTE: Because of hydrolysis, theoretical yields are slightly higher.

From this ratio--180:92--the base may be obtained:

1 lb. total sugars yields 0.5 lb. ethanol

Using the specific gravity of ethanol as 6.6 lbs./gal.:

1 lb. total sugars yields 0.075 gal. ethanol, or

13 lbs. total sugars yields 1 gal. ethanol

II. Alcohol From Grain:

LEGEND TO ACCOMPANY "THE WET MILLING PROCESS OF PRODUCING 200--PROOF ETHANOL FROM CORN".

1. Corn is stored dry (dent corn) in elevated bins.

2. Screens and forced air separate undesirable material, such as cob pieces, from the grain to be processed.

3. Cleaned corn is steeped in water for approximately 40 hours. Sulphur dioxide is bubbled into the mixture to prevent germination. Steeping softens the kernel so that the germ can be removed and other components can be separated later. The steep water contains materials which will contribute to an animal feed by-product, or in volume could be marketed as a growth media.

4. The steeped corn kernel is cracked by revolving plates which contain teeth to remove the germ intact.

5. Germ is "floated" or centrifuged into a press for germ oil recovery. The meal remaining becomes an animal feed constituent.

6. After the germ separation, the remaining fraction of the corn is finely ground, washed, and the hulls separated.

7. Hulls screened from the mass become an animal feed ingredient.

8. Starch and protein now remain. Since the starch has a higher specific gravity than the protein, centrifugation accomplishes an easy separation. The protein becomes the major ingredient of the animal feed by-product, and the starch slurry becomes the feedstock for ethanol production.

   For enzymatic conversion of starch to ethanol, a careful procedure must be followed. The following is only a general description of the process:

9. First, an enzyme of the α-amylase type is added, the pH adjusted, and the diluted starch slurry heated to boiling.

   After the prescribed length of time the mixture is cooled to about 160°F, more α-amylase is added as well as β-amylase, and the temperature maintained for the required length of time.

10. The temperature is reduced to approximately 80°F, yeast added, and the mixture allowed to ferment for 48-72 hours. An 8-10% solution of ethyl alcohol should result.

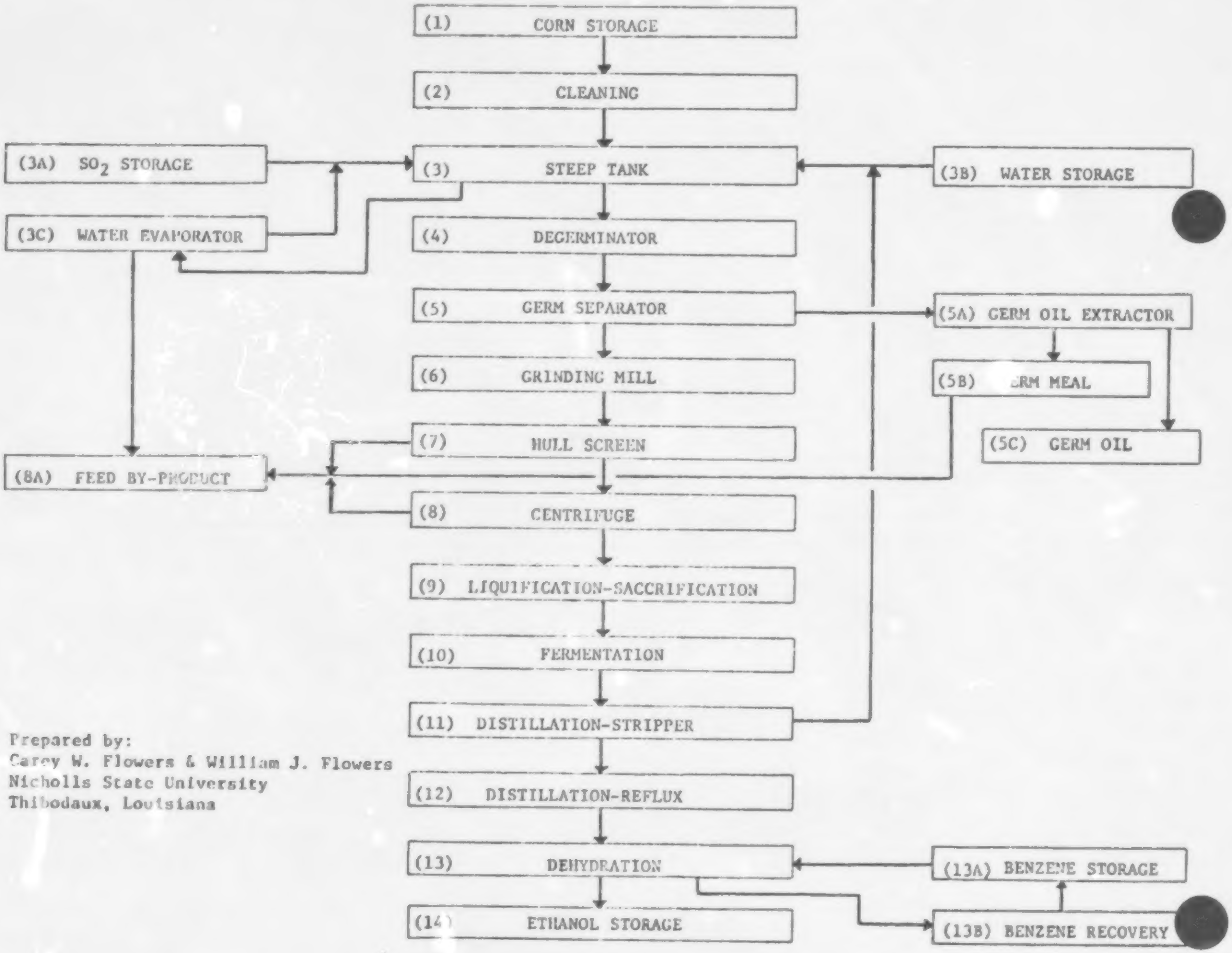
11. This 10% (beer) solution is then distilled at a temperature of near 190°F producing a 50-50 mixture of alcohol and water (100 to 100-proof). The primary purpose of this column is the removal (stripping) of all the alcohol.

12. A second column refines the 100 to 110-proof alcohol to 190 to 192-proof by distillation at a temperature near that of ethanol, about 175°F. This is the maximum proof practicable with distillation. Alcohol and water form an azeotrope at this concentration.

13. Some form of dehydration is necessary to proceed to 200-proof alcohol. One of the most used processes is benzene dehydration, wherein benzene is added to the 190-proof alcohol to make about a 50-50 mixture. The benzene forms an azeotrope (actually two azeotropes) which will distill off at a temperature (about 160°F) below that of ethanol (173°F). The benzene azeotrope can be cooled in such a way as to separate the benzene for recovery.

14. Ethanol should be stored in waterproof containers.

THE WET MILLING PROCESS OF PRODUCING 200° PROOF ETHANOL FROM CORN


(1) CORN STORAGE
(2) CLEANING
(3A) SO_2 STORAGE
(3) STEEP TANK
(3B) WATER STORAGE
(3C) WATER EVAPORATOR
(4) DEGERMINATOR
(5) GERM SEPARATOR
(5A) GERM OIL EXTRACTOR
(6) GRINDING MILL
(5B) ERM MEAL
(7) HULL SCREEN
(5C) GERM OIL
(8A) FEED BY-PRODUCT
(8) CENTRIFUGE
(9) LIQUIFICATION-SACCRIFICATION
(10) FERMENTATION
(11) DISTILLATION-STRIPPER
(12) DISTILLATION-REFLUX
(13) DEHYDRATION
(13A) BENZENE STORAGE
(14) ETHANOL STORAGE
(13B) BENZENE RECOVERY

Prepared by:
Carey W. Flowers & William J. Flowers
Nicholls State University
Thibodaux, Louisiana

FIGURE 7-1

III. Alcohol From Sugar:

TYPES OF FEEDSTOCK: Juices of sugarcane, sweet sorghum, sugar beets, or fruits; syrups, molasses, or massecuites of the above, including corn syrup and corn sweetners; crystalline sugars; or any substance containing sucrose, fructose (levulose), and/or glucose (dextrose).

NOTE: This process will not convert starch or cellulose to alcohol.

BRIEF OUTLINE OF THE PROCESS:

A. Dilution: Add water, if necessary, to achieve 20° Brix (20% dissolved solids) or below.

B. Clarification: With solutions of high suspended solids, some clarification may be desirable at this point. The addition of small amounts of lime (calcium hydroxide) will achieve sufficient clarification. However, fermentable materials could be lost. Many processes recommend omission of this step.

C. Sterilization: Heat the solution to boiling, 100°C (212°F), and maintain for five minutes or adjust the pH to 2.5 or below.

D. Fermentation: Reduce the temperature of the solution to 16° - 32°C (60° - 90°F) and adjust the pH to 4.5. Sulfuric acid may be used to reduce pH, and sodium hydroxide to raise pH. Add yeast and allow to ferment for 12-24 hours (follow enzyme manufacturers' instructions for quantities of yeast, optimum pH, and temperature) maintain optimum temperature with cooling coils as fermentation generates heat. The resulting solution should be approximately 10% alcohol as measured by a proof hydrometer.

E. Distillation: Two stages of distillation are required.

   1. Stripping Column: Distillation at a temperature of about 95°C (203°F) produces a 100 to 110-proof (50% - 55%) alcohol and water solution.

   2. Reflux Column: Distillation of the mixture resulting from Step 1 proceeds at about 79°C (176°F) to produce 190 to 192-proof (95% - 96%) alcohol.

F. Dehydration: For 200-proof (100% alcohol) a dehydration step is necessary. The most used method today is: add 50% by volume benzene to the 190-proof alcohol and distill from 65°C (149°F) through 72°C (162°F). 200-proof remains after distillation of the benzene - water "azeotrope".

ADDITIONAL DISCUSSION OF ALCOHOL FROM SUGAR RELATED FEEDSTOCK

TYPES OF FEEDSTOCK: This method is restricted to substances which contain only simple hexose molecules like fruit sugar (fructose) or the uncomplicated sucrose, which contains one fructose molecule joined with one glucose molecule. Yeast is not capable of breaking down long chains of hexoses as in starch or cellulose. Other enzymes must be used to convert these to simple hexoses.

Feedstocks containing both starch and sugars must be treated with the same process as starch alone.

Mixtures of sugars and finely pulverized cellulose may be processed with the sugar method. However, the cellulose will not be converted to alcohol.

A. Dilution: Dilution is a most important step to avoid waste of valuable feedstock. The total sugar content of the material must be determined at this point and dilution according to the following formula must plan for no more than a 10% by volume alcohol solution when fermentation is completed. A 10% concentration of alcohol begins to kill the yeast and appreciably slow fermentation. Insufficient dilution results in unfermented feedstock being lost in the process.

	$C_6H_{12}O_6$	$\longrightarrow$	$2C_2H_5OH$ +	$2CO_2$ +	
			Ethyl Alcohol	Carbon Dioxide	Heat
Weight Ratio	180		92	88	
	180 lbs.	$\longrightarrow$	92 lbs.		

Using a density of 6.6 lbs./gal. for ethanol, one pound of total sugars produces 0.08 gal. ethanol.

Practically (95% efficiency), about 13.5 lbs. of total sugars produce one gal. of ethanol.

EXAMPLE:

For diluting a blackstrap molasses which contains 55.5% total sugars, each 100 lbs. of feedstock would require 55.5 ÷ 13.5 or 4.2 x 9, or 37.8 gallons of water, to insure a 10% solution of alcohol after fermentation. 37.8 gallons of water + 4.2 gallons of ethanol = 42.0 total gallons.

B. Clarification: Cane or sorghum juice when freshly extracted contains small particles of the stalk which can be removed at this stage by adding lime. This will carry some fermentables with it. If the particles do not interfere with the processing, no clarification should be done.

C. Sterilization: Naturally present on most feedstock material are enzyme-producing organisms which can cause products other than ethanol to be formed. Unwanted organisms are destroyed by heat or acid and then the yeast of the genus saccharomyces is introduced, which produces ethanol. Yeast can be purchased from bakers in cake or dry form.

D. Fermentation: Almost all yeast are destroyed by temperatures above 32°C (90°F) and require an acid pH for optimum action. Certain nutrients are also needed by yeast for survival, but excessive minerals can be lethal. Enzyme manufacturers guidelines should be followed and they vary with strains of yeast.

E. Distillation: There are few differences in distillation techniques of alcohol made from different feedstocks. One may occur in the amount of solids entering the first column. Some engineering modifications may be necessary at this point. However, the process is the same and 190 to 192-proof alcohol is the maximum, in all cases, which can be made by standard distillation because of the "azeotrope" formed by the water and alcohol at a higher concentration of alcohol. The alcohol and water no longer vaporize at different temperatures, making further separation impossible by this method.

NOTE: Stillage from sugar-related feedstock alcohol production contains insignificant amounts of protein and is not used as an animal feed. In fact (even though it contains some minerals such as calcium, nitrogen, phosphorus, magnesium and potassium), the tremendous volumn (10-12 gallons per gallon of alcohol produced) and the high BOD make it a pollutant which must be dealt with before its release to the environment.

F. Dehydration: For use in gasohol this step is necessary, but for use as pure alcohol (not mixed with gasoline), no dehydration is needed. Many reports indicate that 160-proof alcohol is satisfactory for use in modified internal combustion engines.

Source: Carey W. and William J. Flowers
Nicholls State University
Thibodaux, Louisiana 70310

IV. Carbohydrates and Fermentable Sugars

Carbohydrates are any of various compounds comprised of carbon, hydrogen, and oxygen. Commonly, these are formed by green plants through photosynthesis although they can also be synthesized from other substances. In the biological realm, carbohydrates are used to store solar energy until required by the organism. Animals and plants that are not capable of photosynthesis cannot produce their own energy resource and thus derive the energy for metabolism directly or indirectly from those that do. Yeasts, which do not possess the photosynthetic capability, derive their energy from specific types of carbohydrates called fermentable sugars.

The most important carbohydrates are sugars, starches, cellulose, and related substances. Starch and cellulosic compounds are polymeric molecules made up of repeating basic units called monomers. These monomers are joined together by a chemical bond called a glycosidic link.

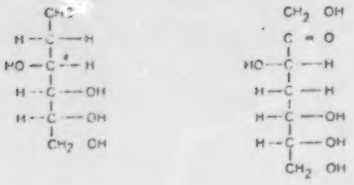
Carbohydrates can be divided into three basic classes: (1) the monosaccharides, (2) the disaccharides, and (3) the polysaccharides. Although each is obviously comprised of successively more of the same basic unit or units, their differences are notable.

A. Monosaccharides

A large portion of the naturally occurring saccharides contain five or six carbon atoms (pentoses and hexoses). When dry, these are colorless crystals, some of which taste sweet. The two most common monosaccharides are glucose and fructose (also called dextrose and levulose, respectively). Glucose and fructose are often diagramatically portrayed as straight chain carbon arrangements as shown in Figure 7-1; however, experimental evidence indicates that they exist mainly in cyclic forms such as shown in Figure 7-2.

Glucose and fructose both have the same chemical formula $C_6H_{12}O_6$ but their chemical behavior differs because of the differences in organization of the atoms in the molecule. Since these compounds have the same formula but are distinctly different compounds, they are called isomers.

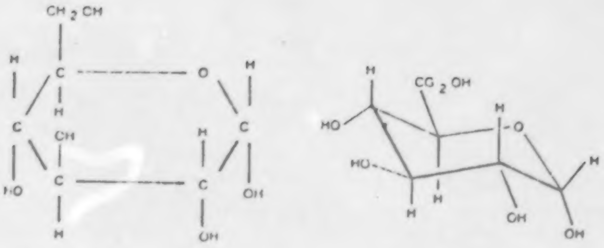
Both glucose and fructose can be fermented to ethanol by the right kind of yeast, but this only results under anaerobic conditions. Glucose and fructose are also readily consumed by other microorganisms, including molds and bacteria. Instead of producing ethanol, these organisms produce a variety of aldehydes, ketones, and organic acids.



GLUCOSE FRUCTOSE

FIGURE 7 - 1

STRAIGHT CHAIN DIAGRAMS OF
FRUCTOSE AND GLUCOSE



SHOWN AS CYCLIC STRUCTURE SHOWN IN 3 DIMENSIONS

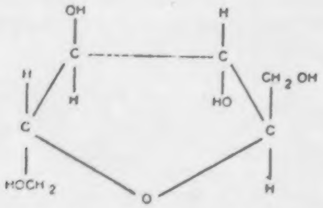


FIGURE 7 - 2

CYCLIC STRUCTURES
OF GLUCOSE & FRUCTOSE

B. Disaccharides

A disaccharide is comprised of two monosaccharides bonded together in a manner that eliminates a hydrogen ion from one and a hydroxyl group (OH-) from the other. The cumulative effect is the elimination of a molecule of water. To break this bond, a hydrogen ion and a hydroxyl group must be added to the respective monomers. Since this is the equivalent of adding a molecule of water, the process is called hydrolysis.

The most common and sweetest-tasting disaccharide is sucrose, a compound made up of fructose and glucose linked together. Sucrose, the most widely used sweetener, is obtained mainly from sugarcane and sugar beets, and is commonly known as table sugar. Figure 7-3 shows a diagram of the sucrose molecule and the glycosidic linkage between the monomeric units.

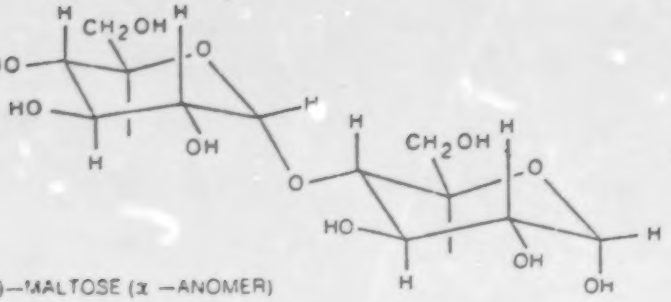
Maltose (malt sugar) which has the same formula as sucrose, $C_{12}H_{22}O_{11}$, results from incomplete enzymatic hydrolysis of starch and is comprised of two molecules of glucose linked together. Both maltose and sucrose are fermentable to ethanol in the presence of certain types of yeast that produce the enzyme necessary to reduce them to their monomeric form.

C. Polysaccharides

Polysaccharides are polymeric carbohydrates of many thousands of monomeric sugar units linked together through glycosidic linkages. In nature, these occur either as food reserves such as starches and glycogen or as structural fibers such as cellulose.

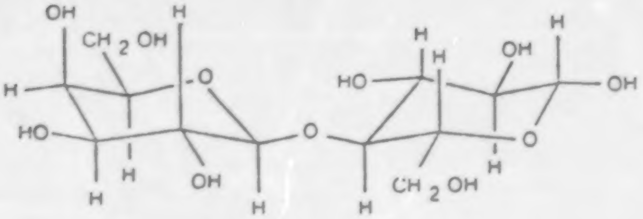
Plant starch is a polymer built upon glucose monomeric units. Its chemical formula is $(C_6H_{10}O_5)_n$. Starch occurs as granules whose size and shape are characteristic of the plant from which the starch is obtained. When intact, starch granules are insoluble in cold water; if the outer membrane has been broken by grinding, the granules slowly swell in cold water. A gel forms when the intact granule is treated with warm water. In hot water, a soluble portion of the starch diffuses through the granule wall and the granules swell to such an extent that they burst.

In general, starch is about 20% amylose, a water-soluble molecule, and 80% amylopectin, a water-insoluble molecule. These two fractions correspond to different carbohydrates of high molecular weight and formula $(C_6H_{10}O_5)_n$. Upon treatment with acid or under the influence of enzymes, the components of starch are hydrolyzed progressively to dextrin (a mixture of low-molecular-weight polysaccharides), (+)-maltose, and finally D-(+)-glucose. (A mixture of all these is found in corn syrup, for example.) Both amylose and amylopectin are made up of D-(+)-glucose units, but differ in molecular size and shape.

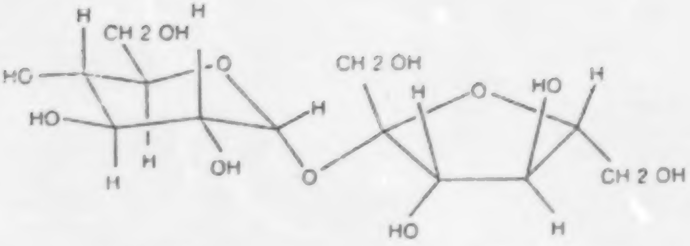

H
CH2OH
H
HO
O
HO
H
H
OH
O
H
CH2OH
H
O
HO
H
OH
H
OH

2 GLUCOSE UNITS

(+)—MALTOSE (α —ANOMER)


OH
CH2OH
H
O
H
HO
H
H
OH
H
O
H
H
OH
H
HO
OH
O
H
H
CH2OH

LACTOSE (β —ANOMER)


H
CH 2 OH
H
HO
O
HO
H
H
H
OH
O
CH 2 OH
H
O
HO
H
CH 2 OH
HO
H

GLUCOSE
AND
FRUCTOSE
UNITS

(+)-SUCROSE

FIGURE 7 - 3

THREE TYPES OF
FERMENTABLE DISACCHARIDES

Figure 7-4 shows several polysaccharides that can be hydrolyzed either with enzymes or mild sulfuric acid, to yield glucose.

Cellulose is the chief component of wood and plant fibers; cotton, for instance, is nearly pure cellulose. It is insoluble in water and is tasteless.

Cellulose has the formula $(C_6H_{10}O_5)_n$. Complete hydrolysis by acid yields D-(+)-glucose as the only monosaccharide. Like starch, cellulose is made up of chains of D-glucose units, each joined by a glycosidic linkage to the number four carbon atom of the next. Cellulose differs from starch, however, in the configuration of the glycosidic linkage. Because of other complex molecules that generally accompany it, cellulose is much more difficult to completely hydrolyze to glucose than starch.

Neither starch nor cellulose can be directly fermented by yeast to produce ethanol. Thus, they must be hydrolyzed to fermentable sugars with either acids or enzymes.

V. Basic Microbiology Concepts Used in Fermentation:

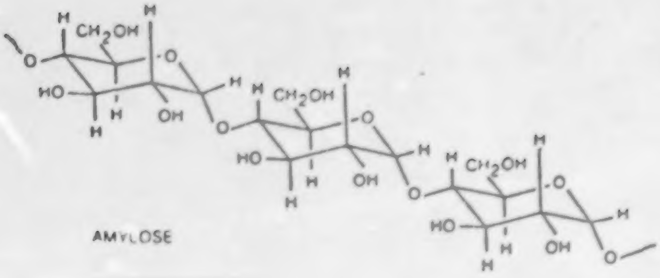
Just as fermentation is the key to successful ethanol production, microbiology is the key to successful fermentation. Yeasts are living microbial organisms. Knowledge of their habits, likes, and dislikes makes it easier to consistently produce beer with a high ethanol content.

A. Enzymes

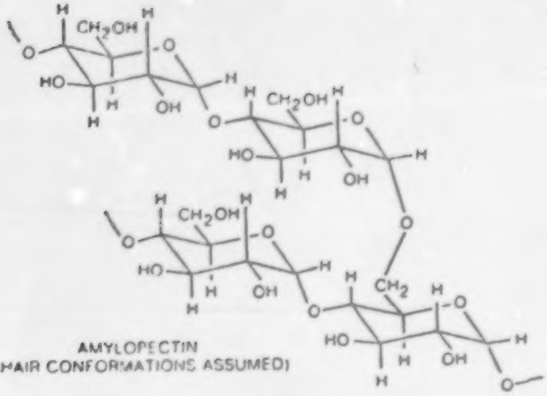
Enzymes are biochemical catalysts. This means that they are principally instrumental in effecting specific chemical reactions but they are not consumed as a result of the reaction. Catalysts serve as mediators between reactants to provide the proper reaction conditions. The enzymes of the yeast metabolism are responsible for conversion of glucose to ethanol. In fact, it is possible, although not very practical, to produce ethanol using only the enzymes from the yeast with no living yeast cells present.

Enzymes are proteins, which, in turn, are long chain polymers of amino acid residues. The surface of each enzyme contains various chemical groups that can react with small molecules. These serve to give enzymes a high degree of specificity. A specific enzyme will combine with only one molecule or a very few kinds of molecules. The molecule with which an enzyme will react is called its substrate. The binding of the substrate (S) to an enzyme (E) results in an enzyme-substrate complex, according to the reversible chemical reaction:

$$E + S \rightleftarrows ES$$

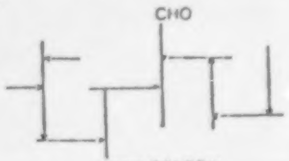


AMYLOSE

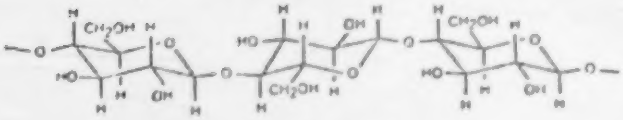


AMYLOPECTIN
(CHAIR CONFORMATIONS ASSUMED)

SCHEMATICALLY THE AMYLOPECTIN MOLECULE IS BELIEVED TO BE SOMETHING LIKE THIS



AMYLOPECTIN



CELLULOSE

FIGURE 7 - 4

POLYSACCHARIDES THAT CAN BE
HYDROLYZED TO YIELD GLUCOSE

This complex serves to activate the substrate so that a chemical reaction can occur. The formation of a product (P) releases the enzyme in its original form, according to the reaction:

$$E\ S \longrightarrow E + P$$

The naming of enzymes is generally done according to the substrates that they cause to react or for the reaction that they catalyze. Customarily, the suffix "-ase" is added to the major part of the substrate name. Thus, a "cellulase" is an enzyme that catalyzes the hydrolysis of cellulose. The enzyme that works with urea is urease; arginine is acted upon by arginase, and so on.

Figure 7-5 shows how the first enzyme used in the process of converting glucose to ethanol serves to bring glucose and adenosine triphosphate (ATP) together so a phosphate group can be transferred to the glucose.

Many enzymes need to be accompanied by certain organic substances called cofactors or coenzymes. These coenzymes generally act as acceptors or donors of functional groups or atoms that are added to or removed from the molecule. This is loosely comparable to a mechanic and his helper in the classic "here-hold-this-a-minute" situation while tearing apart an engine. For example, the enzymes responsible for reduction of glucose to ethanol require the presence of a chemical called adenosine triphosphate and nicotinamide adenine dinucleotide, respectively known as ATP and NAD. ATP serves as a supplier of phosphate groups required to produce the high energy bonds for energy transfer, and NAD serves as a transfer agent for hydrogen ions.

The enzymes responsible for the fermentation of starch to ethanol include hydrolases (enzymes that hydrolyze starch), polysaccharide phosphorylases (which add phosphate to glucose), oxidases, dehydrogenases, decarboxylases isomerases, and others.

Enzymes, although not living organisms, are sensitive to both temperature and pH. The maximum temperature an enzyme can withstand without inactivation is dependent on conditions such as pH, substrate presence, and ionic strength.

Enzymes can be inhibited by compounds that compete with the substrate or by the presence of heavy metal ions such as silver, mercury, and lead.

The enzymes necessary to break down starch to simple sugars are called carbohydrases or amylases. In the past, and even to some extent in current literature, the term diastase is used to refer collectively to the amylolytic enzymes, principally alpha- and beta-amylase and limit dextrinase. In grain mashes, the amylases are used to hydrolyze starch to produce fermentable sugars.

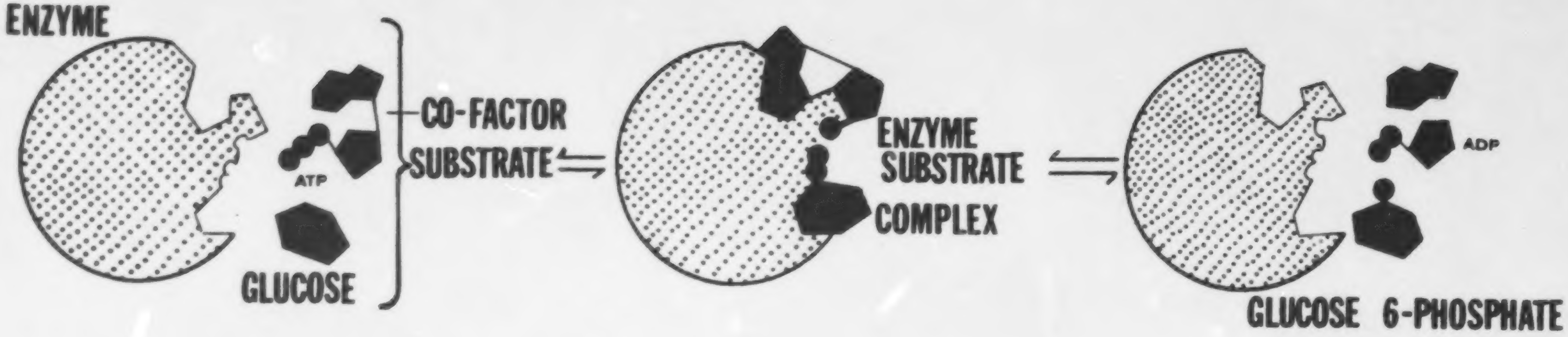

ENZYME
CO-FACTOR
SUBSTRATE
ATP
GLUCOSE
ENZYME SUBSTRATE COMPLEX
ADP
GLUCOSE 6-PHOSPHATE

FIGURE 7-5

ENZYME CONVERTING GLUCOSE TO GLUCOSE 6-PHOSPHATE

Specific enzymes are used to break down the starch molecules. Alpha-amylase is used to open the skin of the starch cell. It randomly hydrolyzes the a-1, 4-glucosidic linkages of starch producing long chain, water soluble sugar called dextrins. As this occurs, the viscosity of gelatinous starch is rapidly reduced. As a consequence, alpha-amylase is commonly referred to as the "liquefying enzyme".

Alpha-amylase does not hydrolyze the a-1, 6 branches in the amylopectin, so another enzyme called gulcoamylase is used to reduce the dextrins to glucose. Glucoamylase not only can hydrolize the a-1, 6 branches of amylopectin, but it also liberates individual glucose units at the 1,4 bond beginning at the nonreducing end of the dextrin. Because glucoamylase is capable of rapidly achieving complete breakdown of dextrins to fermentable sugar, it is commonly called the saccarifying enzyme.

B. The Glycolytic or Embden-Meyerhoff Pathway

The production of ethanol by fermentation of glucose is often expressed in simplified form as:

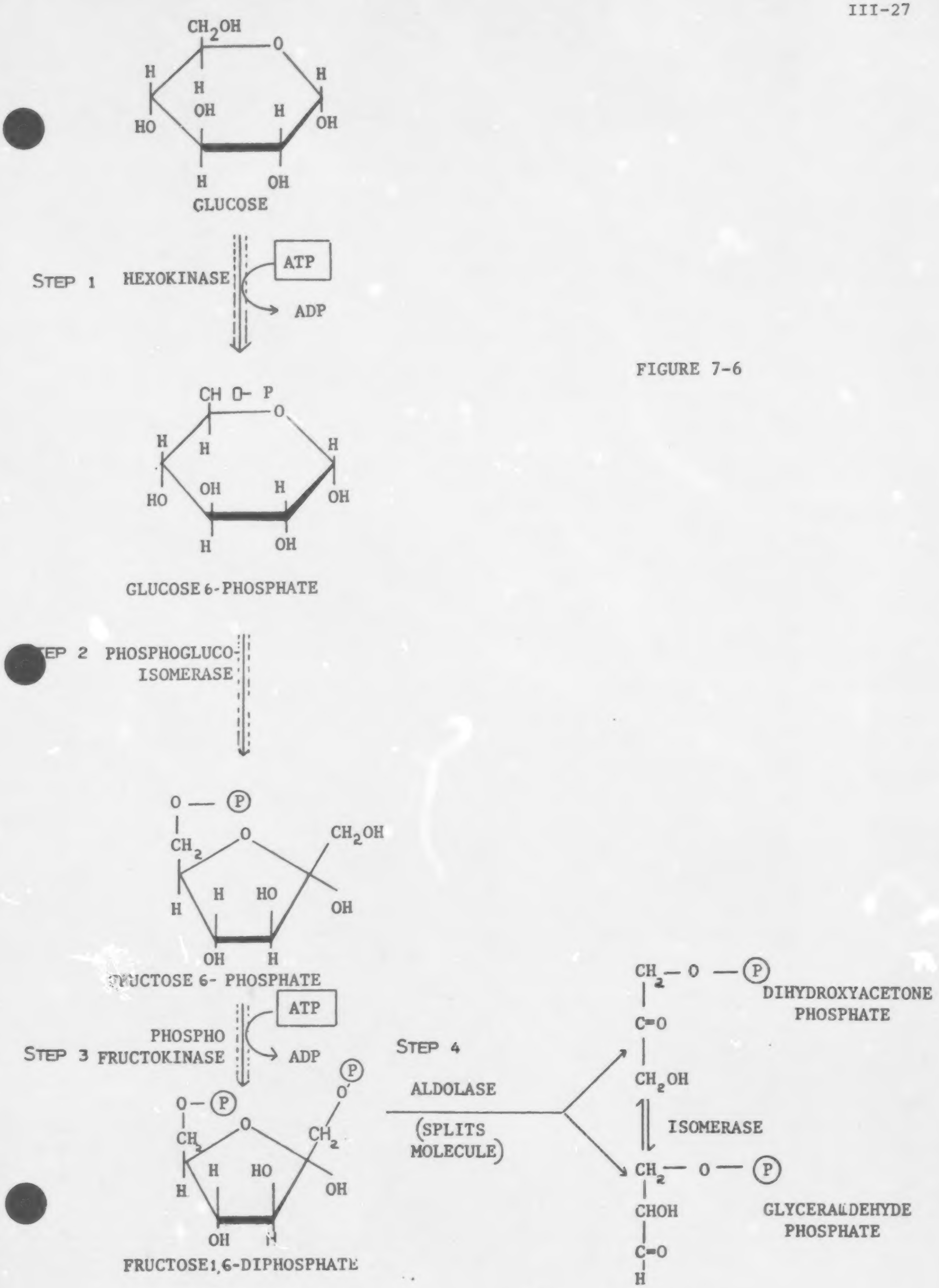
$$C_6H_{12}O_6 \ + \ \text{yeast} \longrightarrow 2C_2H_5OH + 2CO_2 + \text{heat.}$$

Although this expression is a concise summary of the starting materials and the products, it is not a clear portrayal of the sequence of events that actually occurs. The simplification that the summary reaction represents has occasionally led neophyte ethanol producers to assume that fermentation is a trivial exercise. In actuality, it is the basis of ethanol production; the point at which the entire process either succeeds or fails.

The enzymatic conversion of glucose to ethanol requires 12 distinctly separate steps. As shown in Figure 7-6, in the first step an enzyme called hexokinase mediates the addition of a phosphate group from ATP to the glucose molecule. In the second step an isomerase mediates the conversion from glucose-6-phosphate to fructose-6-phosphate. Once this conversion is complete, a second phosphate group can be added to the molecule by an enzyme called a phosphofructokinase to make fructose 1,6 diphosphate. The fourth enzyme is called an aldolase and its purpose is to split this six-carbon molecule into two three-carbon molecules called dihydroxacetone phosphate and glyceraldehyde 3-phosphate.

Because the required molecule for continuation of this path-way is glyceral-dehyde 3-phosphate and dihydroxyacetone phosphate is an isomer of this compound, another isomerase enzyme converts it to the desired form. These three-carbon molecules then undergo an addition of an inorganic phosphate group and the loss of an atom of hydrogen mediated by a dehydrogenase. In this form, a high-energy phosphate bond is formed at the number one carbon

FIGURE 7-6


CH₂OH
O
H
H
OH
H
HO
OH
H
OH
GLUCOSE
STEP 1
HEXOKINASE
ATP
ADP
CH O- P
GLUCOSE 6-PHOSPHATE
STEP 2
PHOSPHOGLUCO-ISOMERASE
O — P
CH₂
CH₂OH
FRUCTOSE 6- PHOSPHATE
PHOSPHO FRUCTOKINASE
STEP 3
ATP
ADP
FRUCTOSE 1,6-DIPHOSPHATE
STEP 4
ALDOLASE
(SPLITS MOLECULE)
CH₂ — O — P
C=O
CH₂OH
DIHYDROXYACETONE PHOSPHATE
ISOMERASE
CHOH
C=O
H
GLYCERALDEHYDE PHOSPHATE

atom. This phosphate group can now be picked off by a kinase and attached to adenosine diphosphate to make adenosine triphosphate. The phosphate is replaced by a hydroxyl group (OH).

In the seventh step, an enzyme called a mutase transfers the phosphate group from the number three carbon atom of the molecule to the number two carbon atom of the molecule. After this transformation, an enzyme called an enolase removes a hydroxyl group from the number three carbon atom and a hydrogen from the carbon atom containing the phosphate group forms another high-energy phosphate bond. The enzyme pyruvate kinase mediates the removal of this phosphate group by the reaction ADP ATP, which leaves a molecule of pyruvate.

Pyruvate is transformed to carbon dioxide and acetaldehyde via an enzyme called pyruvate decarboxylase. The final step to ethanol occurs when a dehydrogenase transfers a hydrogen ion from NADH to acetaldehyde making ethanol.

Up to the production of pyruvate, the glycolytic sequence is the same for yeast, lactic acid bacteria, and even the reactions of oxygen-deficient muscles. However, muscles and lactic acid bacteria have an enzyme called lactate dehydrogenase that makes lactate from pyruvate instead of acetaldehyde and carbon dioxide.

C. Yeasts

Yeasts are fungi, naturally occurring in nature to a very broad extent. Yeasts are found in soils, on plants, and on the surface of fruits and vegetables.

1. Of the common genera of yeasts, the most important as far as the production of ethanol is concerned is Saccharomyces. The two most important species of Saccharomyces are Saccharomyces cerivisiae and Saccharomyces carlsbergensis (also known as Saccharomyces uvarium). During fermentation, most Saccharomyces cerevisiae strains rise to the surface of the fermenting wort and thus function as "top yeasts". In contrast, Saccharomyces carlsbergensis forms no head and characteristically settles to the bottom of the wort, thus functioning as a "bottom yeast".

   Both top-fermenting and bottom-fermenting species include many strains of yeast, each with its own distinct properties. These strains are selected for rate of yeast growth, the limit attenuation, and the flocculation characteristics.

Yeast cells have both a cell wall and cell membrane, as shown in Figure 7-7. Other important features of the cell are:

Mitochondria - bacteria-sized, complex internal membrane arrays responsible for energy generation and respiration of the cell

Endoplasmic reticulum - an extensive internal array of membranes responsible for protein synthesis

Golgi bodies - distinct membrane aggregates responsible for secretion of enzymes

Vacuoles - round, membrane-enclosed bodies of low density responsible for food digestion and waste excretion

Nucleus - a large, centrally located membrane containing genetic material

2. Yeast Propagation

Yeast cells of the genera Saccharomyces reproduce by a process called budding, illustrated in Figure 7-8. The process is characterized by four steps: (1) DNA synthesis, which leads to doubling of the genetic material of the cell, (2) division of the nucleus by a process called mitosis, (3) cell division, which involves the formation of a cell membrane separating the two parts of the divided cell, and (4) cell separation, in which the two cells detach from one another.

Factors Affecting Yeast Propagation

The ability of a cell to reproduce itself is strongly dependent on the availability of the required building materials (nutrients). The cell must duplicate its entire genetic structure, so the materials required to form nucleic acids must be available. Among these materials are amino acids, phosphate, and the sugar, deoxyribose (hence Deoxyribo Nucleic Acid-DNA).

Yeast must be supplied with growth factors such as the vitamins thiamine (1 mg/litre), riboflavin, and biotin. Although these are normally present in grains, other worts may require supplements.

The presence of a small amount of dissolved oxygen greatly enhances yeast propagation.

The initial sugar concentration should not be so high that the osmotic pressure of solution is greater than the yeast can bear.

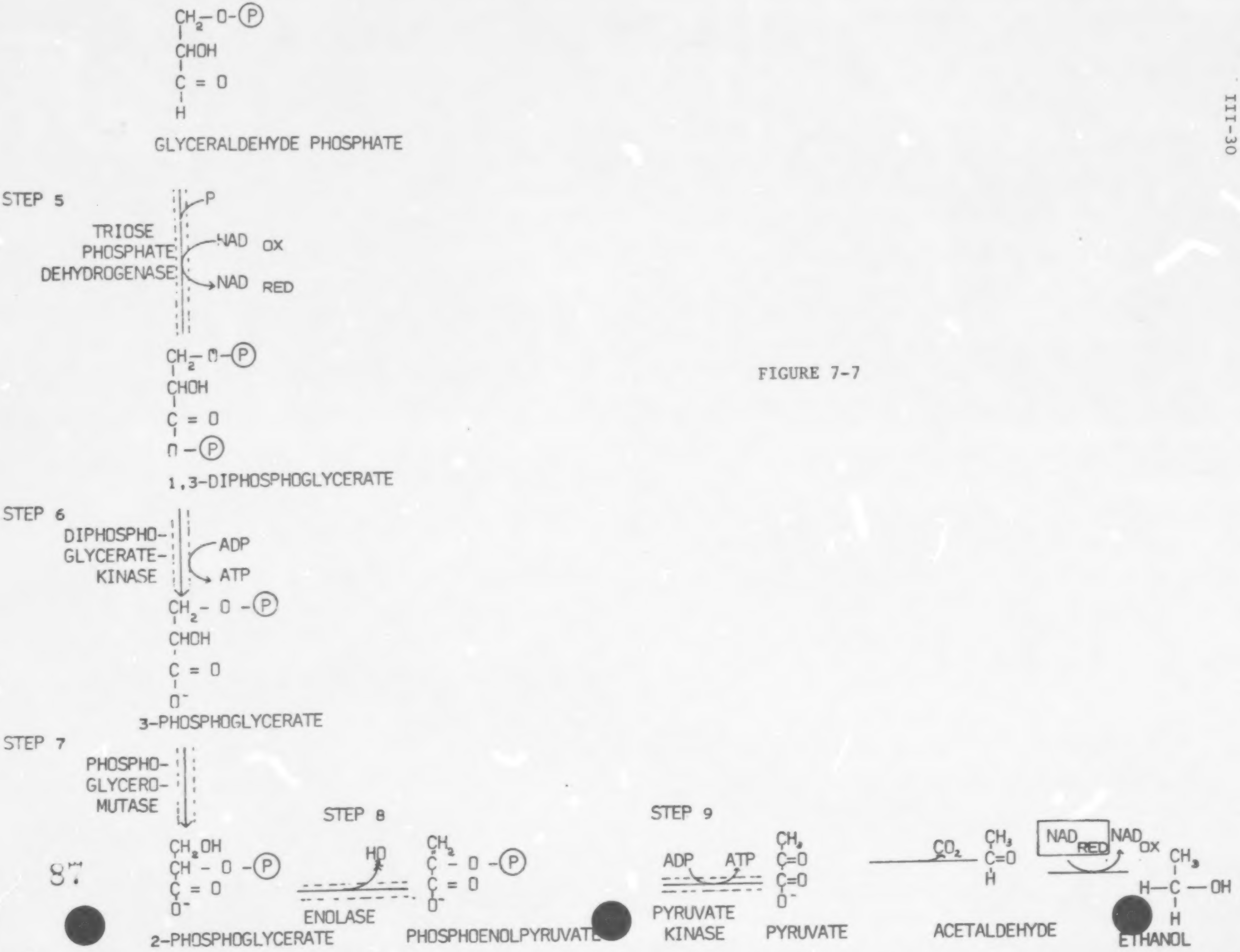

GLYCERALDEHYDE PHOSPHATE
STEP 5
TRIOSE PHOSPHATE DEHYDROGENASE
P
NAD OX
NAD RED
1,3-DIPHOSPHOGLYCERATE
STEP 6
DIPHOSPHO-GLYCERATE-KINASE
ADP
ATP
3-PHOSPHOGLYCERATE
STEP 7
PHOSPHO-GLYCERO-MUTASE
2-PHOSPHOGLYCERATE
STEP 8
HO
ENOLASE
PHOSPHOENOLPYRUVATE
STEP 9
ADP
ATP
PYRUVATE KINASE
PYRUVATE
CO2
ACETALDEHYDE
NAD RED
NAD OX
ETHANOL

FIGURE 7-7

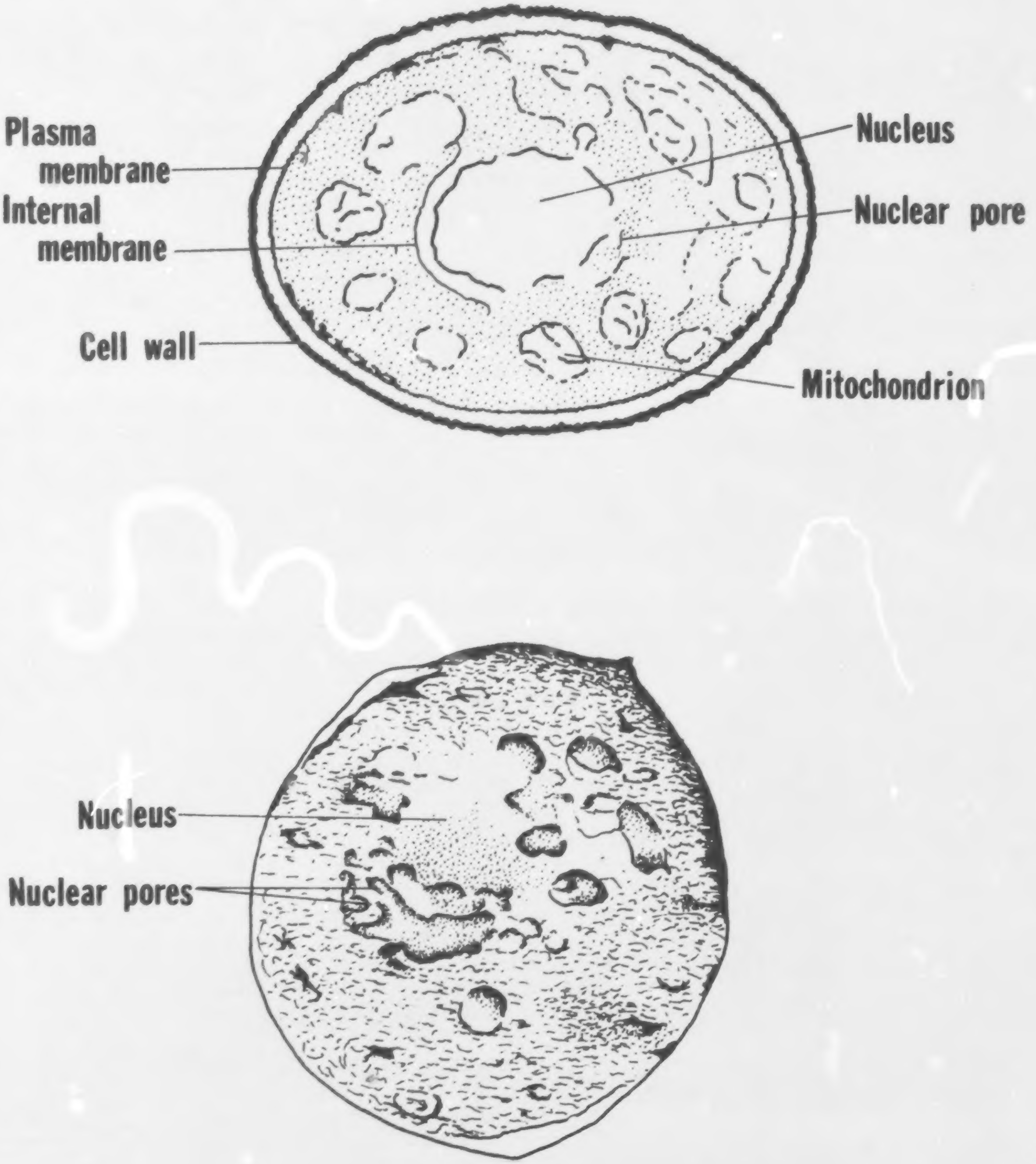

Plasma membrane
Internal membrane
Cell wall
Nucleus
Nuclear pore
Mitochondrion
Nucleus
Nuclear pores

FIGURE 7-8

The presence of small amounts of calcium, magnesium, potassium, zinc phosphorous, and sulfur is required. Although minor amounts of iron and copper are also required, an excess concentration of either will inhibit yeast propagation.

3. Yeast Life Cycle

During the course of a normal fermentation, the yeast cells go through the 4 growth phases illustrated in Figure 7-9; lag phase, exponential phase, stationary phase, and death phase.

When a microbial population is inoculated into a fresh medium, growth does not begin immediately. The period of suspended growth is called the lag phase and the length of time elapsed depends on the similarity of the medium and the culture the inoculum was taken from. These similarities not only include the type of substrate, concentration, pH, temperature, and nutrient composition but also the phase of growth in the initial culture.

An inoculum taken during the exponential growth phase will continue in exponential growth if the medium has basically the same conditions as the inoculum. An inoculum taken during the stationary phase requires a lag period before exponential growth resumes regardless of the similarities between the medium and the growth culture.

A lag occurs when an inoculum consists of cells that have been damaged by heat treatment or chemicals. This lag occurs because of time required to repair the damage. A lag is also observed when a population is transferred from a rich culture medium to a poorer one. Since the cells must have a complete complement of enzymes to synthesize its essential metabolites, time is required for synthesis of the new enzymes.

The exponential phase occurs when yeast begins multiplying. Each cell divides to form two daughter cells, each daughter cell in turn divides to produce two more new cells. With each generation, the population doubles. The rate of growth is expressed in generation time or doubling time, which is the time required for the population to double. One of the characteristics of exponential growth is the fact that the rate of increase in cell number is initially slow but increases at ever faster rates. As a result, the increase in cell numbers of the later growth stages is virtually explosive.

Under optimal conditions the growth rate of different organisms varies considerably. In general, primitive bacteria that do not have a defined nucleus (procaryotic) grow faster than yeast which

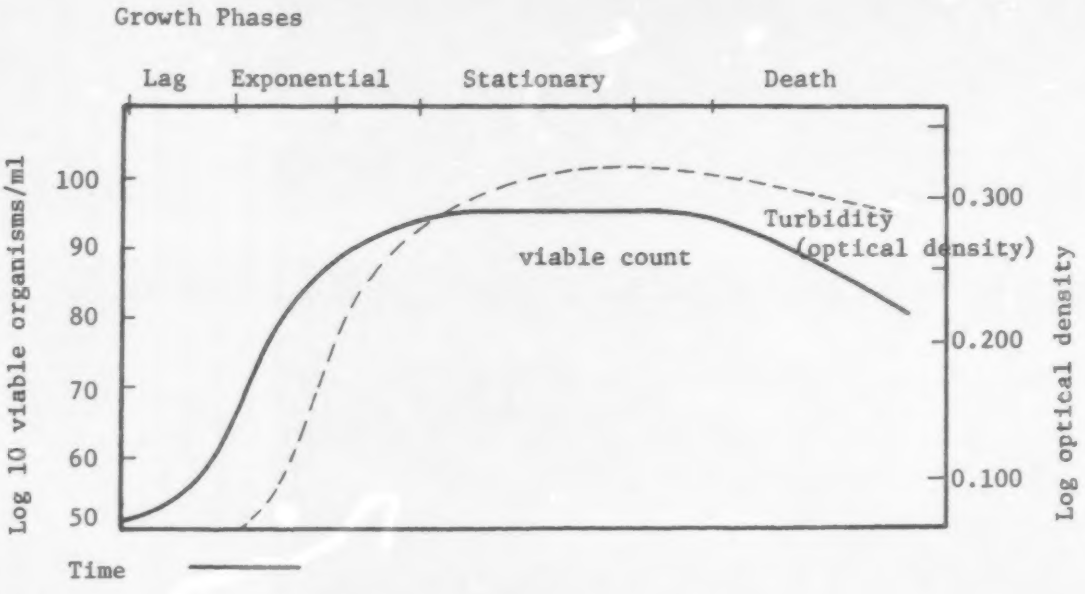


FIGURE 7-9 GROWTH PHASES OF YEAST

do have defined nucleus (eucaryotic). Yeast, as expected, multiplies less rapidly than the bacteria it must compete with. Thus, it is common to give the yeast a headstart by sterilizing the wort to kill the competing bacteria.

In a culture with a finite resource of substrate and nutrients, the growth rate cannot continue indifinitely. The limitation on growth usually occurs as a result of exhaustion of an essential nutrient or because of the accumulation of some metabolic product that is toxic to the yeast. This self-induced growth cessation is called the stationary phase.

Gradually, as the concentration of ethanol increases, the number of dying and dead cells exceeds those that are viable. This can occur either as a result of the toxicity of ethanol (which occurs at around 12% ethanol by volume) or as a result of depletion of the sugar in solution. This phase is called the cell death phase.

D. Antibiotics, Antiseptics, and Thermal Sterilization

An antibiotic is a chemical that kills or inhibits the growth of microorganisms. Antiseptics are germicides that can be used on the skin or to control contamination on surfaces used in the preparation of foodstuffs or animal feeds. Thermal sterilization is accomplished by raising the temperature of the wort to a point where cells are damaged by inactivation of the chromosomal material, breakdown of their proteins, or simply bursting their membranes.

Antibiotics are generally classed according to the organism they kill. Bacteriacides kill bacteria; fungicides kill fungi; and algicides kill algae. Agents with a broad spectrum of target organisms are simply called germicides.

While many microorganisms can stand very high temperatures, almost all can be killed by exposure to a temperature of 250°F for at least 10 to 15 minutes. However, pressurized equipment is necessary to raise the temperature of an aqueous solution past 212°F without completely evaporating it. Many operations cannot justify the expense and complexity attendant to elevated operating pressure.

Fortunately, merely raising the temperature of a solution to boiling and holding there for 15 minutes to one-half hour usually suffices to reduce microbial populations to within acceptable levels. Although this method is ineffective for killing thermally resistant spore-forming bacteria, these bacteria are generally strict anaerobes. Thus, the oxygen used to stimulate yeast propagation effectively inhibits their growth.

E. Water Activity

Water activity is a measure of the availability of water for participation in a biochemical process. The lower the water activity, the more work a cell must perform to extract water from solution. Thus, a cell in a solution with low water activity grows slower with lower total yield than one in a solution with high water activity. Consequently, it is obvious that high water activity is desired to stimulate yeast metabolism and hence ethanol production.

The factors that affect water activity are almost wholly associated with the amount, type and characteristics of substances dissolved in the water. Figure 7-10 shows the water activity of various solutions as a function of concentration of the solute.

Because the solute concentration on the inside of the cell is greater than the concentration in the medium, water in the medium has a strong tendency to flow through the cell membrane into the cell. If the solute concentration in the medium external to the cell is increased above that inside the cell, the water inside the cell will tend to flow out. Under these conditions the cell can only obtain water for growth by increasing its internal solute concentration. Some organisms are more capable of this than others and can grow at lower water activity values. Saccharomyces can generally not tolerate water activities lower than 0.85. The effect of solute concentration on water activity is often considered to be due to its effect on osmotic pressure. Thus, organisms that can stand high concentrations of solute are considered osmotolerant. The few organisms that actually function better at high concentrations of solute are called osmophilic

FIGURE 7-10

WATER ACTIVITY OF VARIOUS SOLUTES

Water Activity	NaCl g/100 ml H_2O	Sucrose g/100 ml H_2O	Glycerol g/100 ml H_2O
.995	.87	0.92	0.26
.980	3.5 (Sea Water)	3.42	1.0
.960	7	6.5	2.0
.900	16.2	14 (Maple Syrup)	5.1
.850	23 (Great Salt Lake)	20.5 (Saturated)	7.8
.800	30 (Saturated)		10.5
.700			16.8
.650			20.0

ALCOHOL FUEL PRODUCTION

MODULE IV - ENGINEERING

I. Introduction:

For purposes of ethanol production, the feedstock (or beer) produced by the fermentation process may be considered a binary (two-component) mixture of water and ethanol which will mix in all proportions. Minor amounts of fusel oils, amyl alcohols, proteins and other chemicals are also present in the beer, but they may be disregarded.

The physical relationships that exist between water and alcohol depend mainly on pressure, temperature, and composition.

Pressure, in most cases of this discussion, can be considered to be atmospheric. Temperature and composition will be the two dependent variables that an attempt will be made to control.

Temperature may be recorded in Fahrenheit degrees or Celsius (Centigrade) degrees. Since technical references may report temperatures either way, we should be able to convert from one to the other. On the Fahrenheit scale, the difference between the freezing point (32°) and the boiling point (212°) of water is 180 degrees. On the Celsius (Centigrade) scale the difference between the freezing point (0°) and the boiling point (100°) of water is 100 degrees. Since it takes 180° of Fahrenheit and only 100 degrees of Celsius to cover the same distance between the freezing and boiling points of water, a Fahrenheit degree obviously is smaller than a Celsius degree.

The ratio is: 180/100 or 1.8/1

It takes 1.8 Fahrenheit degrees to make one Celsium degree. To convert from one to the other, it is necessary to start where both read the same at minus 40°.

To convert, use the following procedure:

1. Add 40° to the temperature to be converted.
2. Then, if going from Fahrenheit to Celsius, divide by 1.8; if going from Celsius to Fahrenheit, multiply by 1.9.
3. To complete the conversion, subtract the 40° originally added.

II. Objectives:

Upon completion of this module the student will be able to:

A. Identify terms and definitions related to engineering.

B. Cite the properties of ethanol, including composition, temperature-composition relationships, and azeotropes.

C. Describe distillation, to include equilibrium flash, simple pot still, batch still with separating column, and continuous distillation processes.

D. Explain how to decide what size the still should be and what materials are suitable for use.

III. Instructional Materials:

A. Laboratory distillation material: glassware, stirring rods, beakers, flasks columns glass beads, etc.

B. Laboratory oven

C. Yeast, enzyme, grain, and antibiotics

D. Hotplate and Bunsen burners'

E. Denaturant

IV. References:

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MODULE IV - ENGINEERING

Terms and Definitions:

1. Alcohols - A group of organic chemical compounds composed of carbon, hydrogen, and oxygen.

2. Aldehydes - Any of a class of highly reactive organic chemical compounds obtained by oxidation of primary alcohols, characterized by the common group CHO, and used in the manufacture of resins, dyes and organic acids.

3. Alpha-amylase - Amylase: any of various enzymes that convert starch to sugar.

4. Anhydrous - Free from water and especially water of crystallization.

5. Azeotrope - A liquid mixture which exhibits a maximum or a minimum boiling point relative to the boiling points of surrounding mixture compositions.

6. Azeotropic - In distillation, the mixture of alcohol and water produces a different temperature for boiling than either alcohol or water alone. "Ternary Azeotropic Distillation" - one process by which 190 alcohol can be brought to 200 proof through the addition of a third component.

7. Vrix or Valling Hydrometer - A triple scale wine hydrometer designed to record the specific gravity of a solution containing sugar.

8. Barrel of oil - 42 gallons.

9. BDG - Brewer's Dried Grain.

10. Btu - Quantity of heat required to raise temperature of one pound of water one degree farenheit (about the heat of burning one match); abbreviation for British thermal unit.

11. Calorie - The quantity of heat required to raise the temperature of one gram of water one degree Centrigrade.

12. Catalyst - A substance, usually present in small amounts relative to the reactants, that modifies, especially increases, the rate of a chemical reaction without being consumed in the process.

13. Catalyse - To modify the rate of a chemical reaction as a catalyst.

14. Cooker - A tank or vessel designed to cook a liquid or extract or digest solids in suspension. The cooker usually contains a source of heat and is fitted with an agitator.

15. Condenser - A component of a distillation plant used to cool vapors and condense them to liquid. The condenser unit uses a coolant (water) to effect vapor condensation.

16. Critical Temperature - Temperature at which a substance changes from one phase to another. Example: The change from solid ice to liquid water or the change from liquid to gas.

17. Critical Temperature - Is the temperature at which latent heat becomes zero. For water critical temperature is 705.4° F.

18. Denature - The process of adding a substance to ethyl alcohol to make it unfit for human consumption. The denaturing agent may be gasoline or other substances specified by the Bureau of Alcohol Tobacco and Firearms.

19. Dewatering - To remove the water from a substance.

20. Ethanol (ethyl alcohol) - C_2H_5OH, the alcohol product of sugar fermentation which is used in alcohol beverages and for industrial purposes and is proposed for blending with gasoline to make gasohol.

21. Fractional Distillation - A process of separating alcohol and water (or other mixtures).

22. Fusel Oil - An acrid oily liquid occurring in insufficiently distilled alcoholic liquors, consisting chiefly of amyl alcohol.

23. Gasohol - A blend of gasoline and alcohol (usually ethanol) commonly discussed as a product being composed of 90 percent gasoline and 10 percent ethanol.

24. Heat of Vaporization - Heat required to convert a liquid into a gas.

25. Horse Power - A standard unit of power equal in the U. S. to 746 watts.

26. ICE - Internal Combustion Engine.

27. Ketones - Any of a class of organic compounds having a carbonyl group linked to a carbon atom in each of two hydrocarbon radicals and having the general formula $R_1(CO)R_2$, may be the same as R_2.

28. Kilowatt (KW) is 1000 watts or about 1.34 horsepower.

29. Methanol - (Methyl alcohol, also known as wood alcohol) CH_3OH, one of the alcohols which has been proposed for blending with gasoline. However, methanol does not blend as well as ethanol.

30. Osmatic Pressure - Osmosis - the diffusion of fluid through a semipermeable membrane until there is an equal concentration of fluid on either side of the membrane. Pressure is created by concentration of a fluid on one side of a membrane.

31. pH - Is a number designated to understand the degree of alkalinity or acidity of a liquid. The numbers range from 1 to 14. The neutral solution which is neither acidic or alkaline is given a number 7. Higher numbers between 1 to 14 refer to alkalinity. Lower numbers 7 to 1 refer to acidity.

32. Pound of Steam - Reference to the pounds of steam per hour value of generating capacity of boilers or steam generating equipment or use, to indicate the steam output or consumption in pounds per hour.

33. Practical Yield - The amount of product that can actually be derived under normal operating conditions. (i.e. amount of sugar that can normally be obtained from a given amount of starch or the amount of alcohol that normally can be obtained is usually less than theoretical yield.)

34. Producer Gas - A gas used as fuel, generated by passing air with steam over burning coke or coal to yield a combustible mixture of nitrogen, carbon monoxide and hydrogen. Also called "air gas".

35. Rectified Alcohol - Alcohol that has been purified by repeated or fractional distillation thereby increasing the proof.

36. Reflux - A flowing back.

37. Renewable Resources - (Renewable energy) Resources that can be replaced after use through natural means. Example: Solar energy, wind energy, energy from growing plants.

38. Specific Gravity - The ratio of the density of a substance to the density of a substance (as pure water or hydrogen) taken as a standard when both densities are obtained by weight in air.

39. Still - Any apparatus capable of vaporizing and condensing liquids or of separating liquids or vapors from solid materials by means of vaporizing and condensing generally referred to as distillation. For highly technical considerations, this term can also mean any other apparatus used for separating alcohol from liquid or solid materials.

40. Stillage - Spent mash after the alcohol has been removed.

MODULE IV - ENGINEERING

OUTLINE

I. Ethanol Properties

    A. Composition
    B. Temperature Composition Relationships
    C. The Azeotrope

II. Distillation

    A. The Process
    B. Equilibrium Flash Distillation
    C. Batch Differential Distillation

        1. Fractionating Columns
        2. Reflux
        3. The Batch Still with Separating Columns

    D. Continuous Distillation

        1. Internal Make-up of Columns

            a. The Stripper Section
            b. The Rectifier Section

        2. Heat

            a. Requirements
            b. Conservation
            c. Application

III. Sizing the Still

    A. General
    B. Column Height

        1. Packed Column Design
        2. Packing Support Grid

    C. Materials

ALCOHOL FUEL PRODUCTION

MODULE IV - ENGINEERING

I. Ethanol Properties

A. Composition

Ethanol amount in water is measured as proof, volume percent, weight percent, and mole percent. Hydrometers are generally used for measuring proof or volume percent. Proof is twice the volume percent or volume percent is 1/2 the proof reading. For example, 100 gallons of 180 proof (90% ethanol by volume) contains 90 gallons of pure ethanol and 10 gallons of water.

Weight percents and mole percents are generally used in engineering and chemical calculations. Table 2 lists comparative volume, weight, and mole percents.

B. Temperature-Composition Relationships

The boiling point (or bubble point) of water is 212°F (100°C) and that of ethanol is 172°F (77.7°C). It would seem that just raising the temperature of the mixture to 172°F (77.7°C) would be all that is necessary to boil off the ethanol. However, this is not so in a mixture although it would for pure ethanol. In a mixture, the vapor would contain molecules of both the water and the ethanol.

In general, the ethanol (low temperature boiler) will evaporate more rapidly than the water (high temperature boiler). The vapor mixture in equilibrium with the boiling liquid mixture will have a higher percentage of ethanol than the liquid itself. The relative volatility of the water to the ethanol is a direct index of the tendency to separate upon distillation. A high relative volatility indicates easy separation. The relative volatility varies with temperature and pressure. Consequently, varying the pressure or temperature will affect the boiling equilibrium of the mixture. For example, a mixture of 40% ethanol when heated to 82° Centigrade a vapor of about 58% ethanol will be in equilibrium with a liquid containing 30% ethanol.

If the temperature of this mixture is raised to 84° Centigrade a vapor of about 50% ethanol would be in equilibrium with a liquid containing 18% ethanol.

C. The Azeotrope

An important point to note in the boiling diagram of Figure 1 is this:

as the temperature decreases, the vapor line and liquid line converge to form a single line at about 173° and 89.3 mole % (94.5 vol.%) ethanol. This means that from this temperature downward there is no difference between vapor composition and liquid composition. This is the maximum concentration which can be recovered by the distillation of a water-ethanol mixture at normal atmosphere pressure. Mixtures of this kind are called azeotropes.

As a result of the physical and chemical relationships that exist between ethanol and water, a calculation can be made to find the amount of distillate of a given ethanol content that can be expected from a beer of known ethanol content. The following relationship may be used:

$$\text{Gallons of Distillate} = \text{Gallons of Beer} \times \left(\frac{\text{Vol \% of ethanol in beer} - \text{Vol \% of ethanol in bottoms}}{\text{Vol \% of ethanol in distillate} - \text{Vol \% of ethanol in bottoms}} \right)$$

EXAMPLE: How many gallons of distillate containing 94% ethanol by volume can we get from 100 gallons of beer, 12% ethanol by volume. The bottoms will have an alcohol content of 3% by volume.

$$\text{Distillate} = 100 \left(\frac{12 - 3}{94 - 3} \right) = 100 \left(\frac{9}{91} \right)$$

Distillate = 9.89 gallons.

This will leave 100 - 9.89 = 90.11 gallons of stillage of 3% ethanol content.

Conversion Table for Centigrade (Celsius) and Fahrenheit Temperatures.

F°	C°	C°	F°
212	100	100	212
211	99.4	99	210.2
210	98.9	98	208.4
209	98.3	97	206.6
208	97.8	96	204.8
207	97.2	95	203
206	96.7	94	201.2
205	96.1	93	199.4
204	95.6	92	197.6
203	95	91	195.8
202	94.4	90	194
201	93.9	89	192.2
200	93.3	88	190.4
199	92.8	87	188.6
198	92.2	86	186.8
197	91.7	85	185
196	91.1	84	183.2
195	90.6	83	181.4
194	90	82	179.6
193	89.4	81	177.8
192	88.9	80	176
191	88.3	79	174.2
190	87.8	78.5	173.3
189	87.2	78	172.4
188	86.7		
187	86.1		
186	85.6		
185	85		
184	84.4		
183	83.9		
182	83.3		
181	82.8		
179	81.7		
178	81.1		
177	80.6		
176	80		
175	79.4		
174	78.9		
173.3	78.5		
173	78.3		
172	77.8		
171	77.2		
170	76.7		

TABLE 1

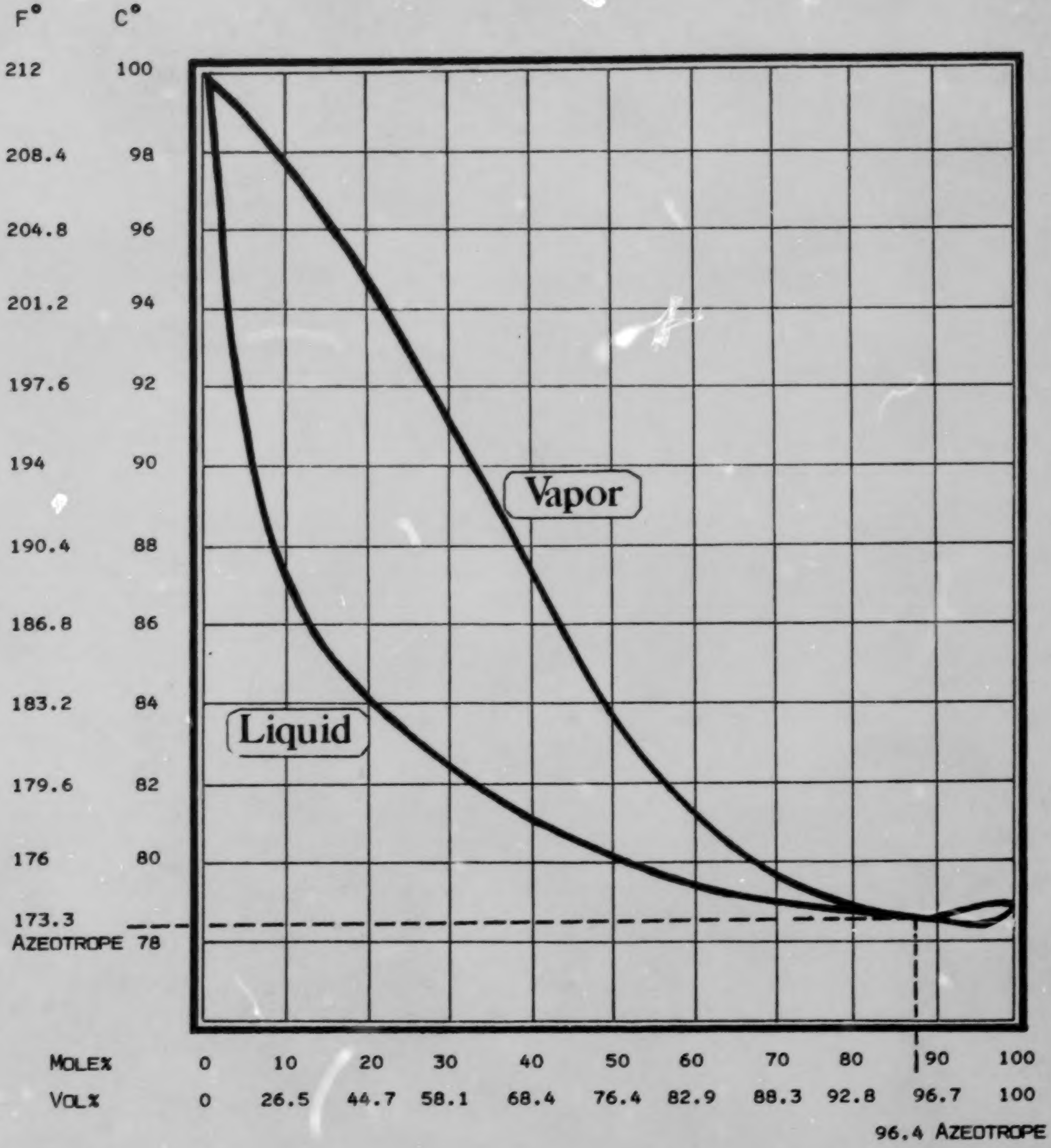
TABLE 2

Table of Volume Percents, Weight Percents and Mole Percents of Ethanol in Water

(Note: Proof is 2 x volume %)

Vol. %	Wt. %	Mol. %	Vol. %	Wt. %	Mol. %
1.00	0.79	0.31	51.00	45.09	24.32
2.00	1.58	0.63	52.00	46.08	25.06
3.00	2.38	0.95	53.00	47.08	25.82
4.00	3.18	1.27	54.00	48.08	26.60
5.00	3.99	1.60	55.00	49.09	27.40
6.00	4.79	1.93	56.00	50.10	28.21
7.00	5.61	2.27	57.00	51.12	29.04
8.00	6.42	2.61	58.00	52.14	29.89
9.00	7.24	2.96	59.00	53.17	30.76
10.00	8.06	3.32	60.00	54.20	31.65
11.00	8.89	3.68	61.00	55.24	32.56
12.00	9.71	4.04	62.00	56.28	33.50
13.00	10.55	4.41	63.00	57.33	34.46
14.00	11.38	4.79	64.00	58.38	35.44
15.00	12.22	5.17	65.00	59.44	36.44
16.00	13.07	5.55	66.00	60.50	37.47
17.00	13.91	5.95	67.00	61.57	38.53
18.00	14.76	6.35	68.00	62.64	39.62
19.00	15.62	6.75	69.00	63.72	40.73
20.00	16.48	7.17	70.00	64.80	41.87
21.00	17.34	7.58	71.00	65.89	43.05
22.00	18.20	8.01	72.00	66.98	44.26
23.00	19.07	8.44	73.00	68.08	45.50
24.00	19.95	8.88	74.00	69.19	46.77
25.00	20.82	9.33	75.00	70.30	48.08
26.00	21.70	9.79	76.00	71.42	49.44
27.00	22.59	10.25	77.00	72.54	50.83
28.00	23.48	10.72	78.00	73.67	52.26
29.00	24.37	11.20	79.00	74.80	53.73
30.00	25.27	11.69	80.00	75.94	55.26
31.00	26.17	12.18	81.00	77.08	56.83
32.00	27.08	12.69	82.00	78.23	58.45
33.00	27.99	13.20	83.00	79.39	60.12
34.00	28.90	13.72	84.00	80.55	61.84
35.00	29.82	14.25	85.00	81.72	63.63
36.00	30.74	14.80	86.00	82.90	65.48
37.00	31.67	15.35	87.00	84.08	67.39
38.00	32.60	15.91	88.00	85.26	69.36
39.00	33.53	16.49	89.00	86.46	71.41
40.00	34.47	17.07	90.00	87.66	73.54
41.00	35.41	17.66	91.00	88.86	75.74
42.00	36.36	18.27	92.00	90.07	78.02
43.00	37.31	18.89	93.00	91.29	80.40
44.00	38.27	19.52	94.00	92.52	82.87
45.00	39.23	20.17	95.00	93.75	85.44
46.00	40.20	20.82	96.00	94.98	88.11
47.00	41.17	21.49	97.00	96.23	90.89
48.00	42.14	22.18	98.00	97.48	93.80
49.00	43.12	22.88	99.00	98.74	96.83
50.00	44.10	23.59	100.00	100.00	100.00

Figure 1. Water-ethanol boiling diagram
(Modified after Rieder and Thompson)



II. Distillation

A. The Process

The process of distillation is used to separate mixtures of compounds or substances by utilizing differences in their boiling points and ease of vaporizing. The separation may be partial or complete. In any case, the relative concentrations of the components in the original mixture is increased in the distillate or the residual mixture (bottoms or stillage).

Distillation processes may be classified according to the number of components in the original mixture as binary, when there are two components; as multicomponent, when there are more than two definable components; and as multicomplex, when the number and individaul components are unidentifiable as compounds. As stated in the beginning, the beer from the fermentation process is a binary mixture of water and ethanol, so we are concerned only with the separation of a binary mixture.

A further classification according to the type of separation may be made as equilibrium and as differential or fractionating.

Then, some processes can be designated as batch or continuous, and as pressure, vacuum, or steam distillations. Almost any combination of these classifications can be utilized to separate water from ethanol. Some of these are more suitable than others to produce a desired result.

B. Equilibrium Flash Distillation

In equilibrium distillation,the liquid phase and vapor phase are in contact at the same temperature and pressure for a period of time to allow some equilibrium to be established between the liquid and vapor phases.

Figure 2 shows the feed as it is pumped through a heater and the pressure is reduced through a valve into a separator which receives the mixture of vapor and liquid. Because of the intimacy of contact between liquid and vapor before separation, the separated streams are in equilibrium. Vapor leaves through the top of the separator and is cooled in a condenser. Liquid may be dumped from the bottom of the separator.

With proper control equipment, this can be made a continuous process which could be used for alcohol distillation. However, the purity of the alcohol would not be as high as from other methods, nor would the system prove efficient.

As an example, oil and gas separator in the oil field works in this way.

C. Batch Differential Distillation (Simple Pot Still)

In this operation, the mixture is put into a pot or kettle and is then heated to its bubble point. Boiling starts and continues as the distillate is continuously removed as a vapor and condensed externally from the still as a liquid product. There will be a gradual increase in boiling temperature as the percentage of ethanol decreases in the liquid. As the amount of distillate increases, the amount of water will also increase. Therefore, if boiling continues, eventually all of the liquid will boil away and the distillate will have the same content as the original liquid, provided there have been no external losses.

1. Fractionating Columns

If a mixture of ethanol and water of low ethanol concentration is heated to its bubble point, vapors will be given off. These vapors will have a higher concentration than the original liquid (Figure 1). If these vapors are then condensed in another container and heat is applied to raise the mixture to the bubble point, the vapors given off in this second step will again have a higher ethanol content than that of the liquid from which it came. A series of steps or stages such as this can produce an ethanol content of the azeotropic percentage in the final stage. Figure 3 illustrates the basic process of successive distillation to increase the concentration of ethanol.

2. Reflux

Each successive stage above produces a vapor richer in ethanol from a liquid richer in ethanol than the previous stage. If part of the liquid of highest ethanol content is put back into the liquid of the different stages, the ethanol content of the liquids will be increased. This will in turn increase the content of the vapor. THIS LIQUID THAT IS RETURNED TO THE DISTILLATION SYSTEM IS CALLED REFLUX. Refluxing will improve the percentage of ethanol in the distillate and increase the amount of distillate recovered.

Because the lighter boiling ethanol is concentrating in the vapor from each successive stage, the temperature decreases from stage to stage and reaches the minimum as the final vapor is produced from the process. Since temperature is a measure of the level of heat energy, it is obvious that heat energy is necessary to the distillation process.

In addition to the heat energy involved in maintaining a temperature differential, an amount of heat energy roughly equivalent to the latent heat of the vapor involved from the last stage must be supplied.

The requirements discussed above and illustrated in Figure 3 have been met by the device called a fractionating column which is shown schematically in Figure 4. Each stage of Figure 3 corresponds to a contact stage commonly called a plate or tray or packing. These provide contact surfaces so that vapor and liquid by intimate contact approach equilibrium in both composition and temperature.

3. Batch Still With Separating Column

The batch still with separating column is suitable for small quantities of raw materials at irregular intervals. As shown in Figure 5, this type consists of the following:

a. A reboiler or kettle of ample volume to receive the charge.

b. A heat source.

c. A separating column consisting of trays, plates, or packing.

d. A condenser or heat exchanger to cool the ethanol.

e. Storage tanks (not shown).

At start up, as heat is applied to the batch to be distilled vapors will be given off when the bubble point of the mixture is reached. At this point, the column is still cool and vapors will begin condensing within the column to provide self-refluxing and enrichment as the column rises to its operating temperature. When operating temperature is reached, vapors will then reach the condensor for condensation, with very little (or none) condensing in the column. At this point, it becomes necessary to reflux a part of the condensate back into the column to provide an ethanol-rich liquid interface for ethanol enrichment of the rising vapors. Unless this is done, the effectiveness of the separating column is impaired or destroyed.

There are two ways of operating this type of still. One method is to operate with a constant reflux ratio. A good ratio for this would be 4 to 1, or four units back into the column for every one unit drawn off. This will result in a distillate of high ethanol content in the beginning tapering off to a distillate of lower ethanol content as time goes on. This is similar in operation to the simple pot still discussed previously, the difference being that with the batch still and column the amount of high ethanol distillate will be greater. Therefore, it is a more efficient distillation system.

The other method of operation is to increase the reflux ratio from about 4 to 1 to about 16 to 1 over a period of time. In this

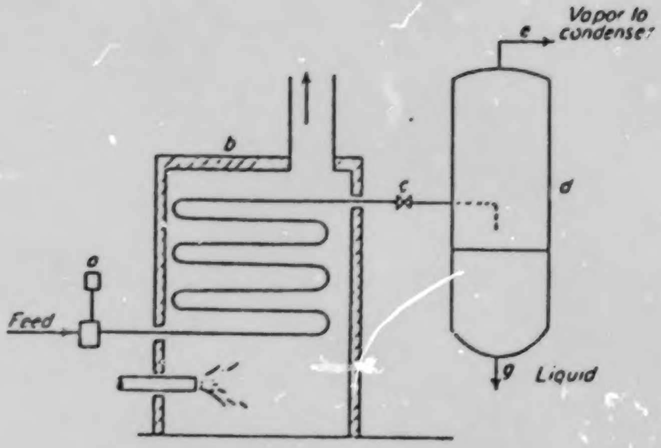
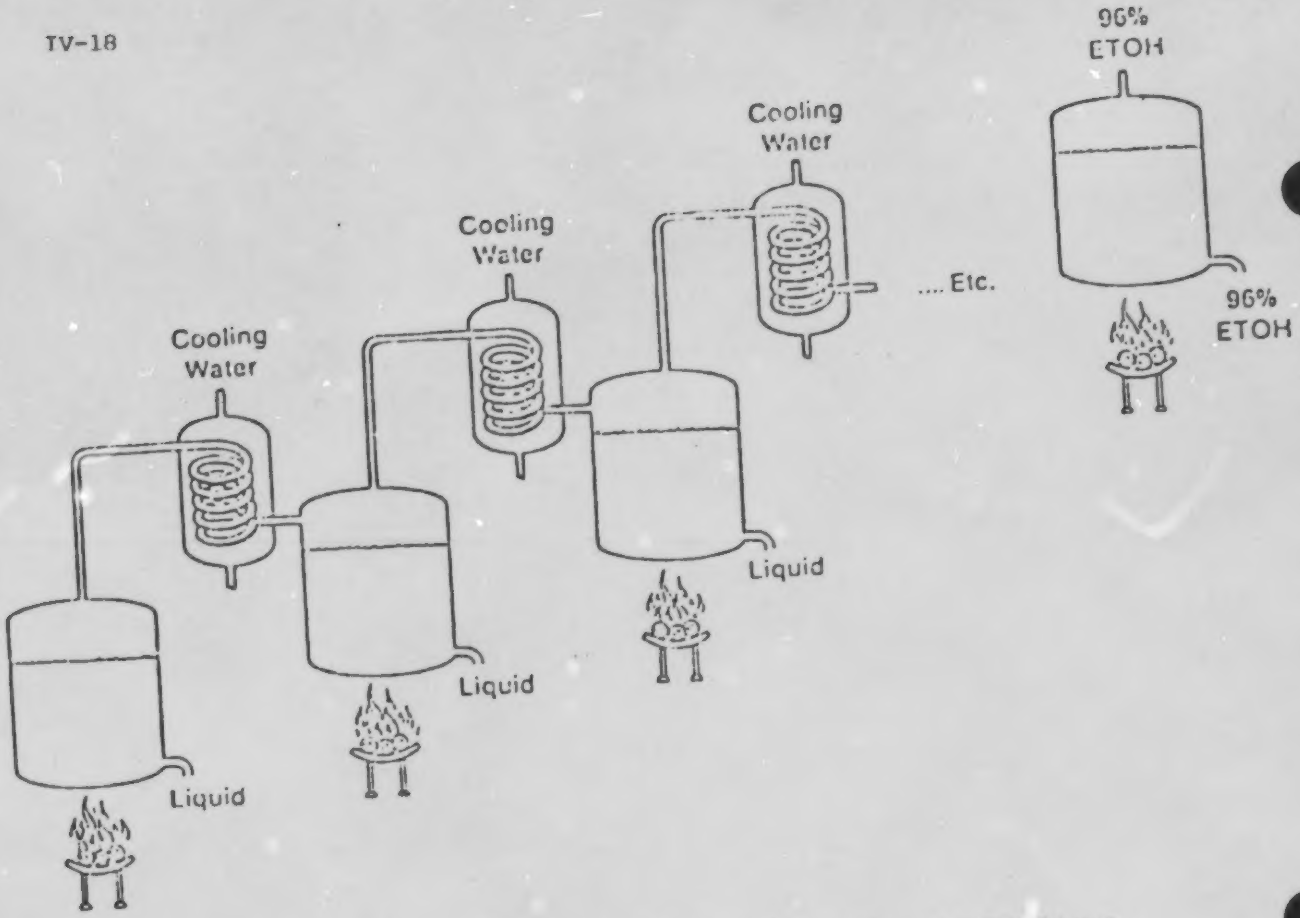
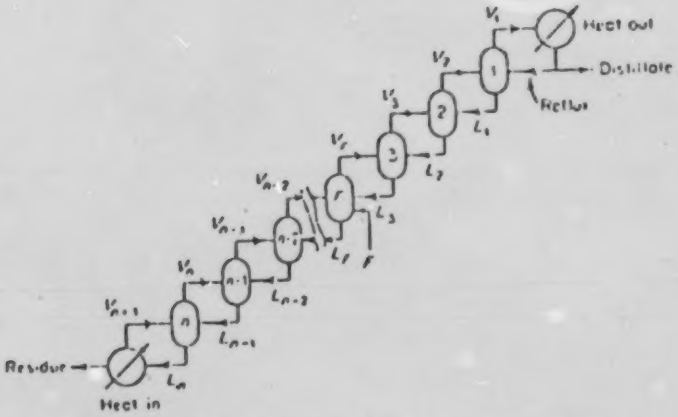


Figure 2. Diagram of a Flash Distillation Unit. (After McCabe and Smith) (Feed is pumped by pump a through heater b, and the pressure is reduced through valve c. An intimate mixture of vapor enters the vapor separator d, in which sufficient time is allowed for the vapor and liquid portions to separate. Because of the intimacy of contact of liquid and vapor before separation, the separated streams are in equilibrium. Vapor leaves through line e and liquid through line g.)


96%
ETOH
Cooling
Water
Cooling
Water
Cooling
Water
.... Etc.
96%
ETOH
Liquid
Liquid
Liquid

A. Basic Process of Successive Distillation to Increase Concentration of Ethanol
(After fuel from farms)


V_1
Heat out
V_2
1
Distillate
Reflux
V_3
2
L_1
V_f
3
L_2
V_{n-2}
f
L_3
V_{n-1}
n-2
L_f
F
V_n
n-1
L_{n-2}
V_{n+1}
n
L_{n-1}
Residue
L_n
Heat in

B. Schematic fractional distillation process.
(After Van Winkle)

Figure 3. Successive Distillation

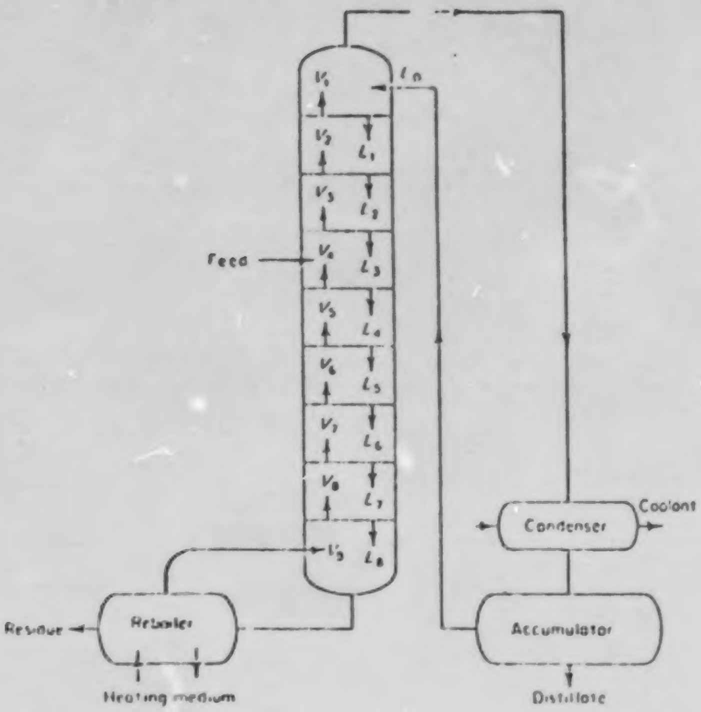

V1
L0
V2
L1
V3
L2
Feed
V4
L3
V5
L4
V6
L5
V7
L6
V8
L7
V9
L8
Condenser
Coolant
Reboiler
Residue
Heating medium
Accumulator
Distillate

Fig. 4. Conventional Fractionating Column
(After Van Winkle)

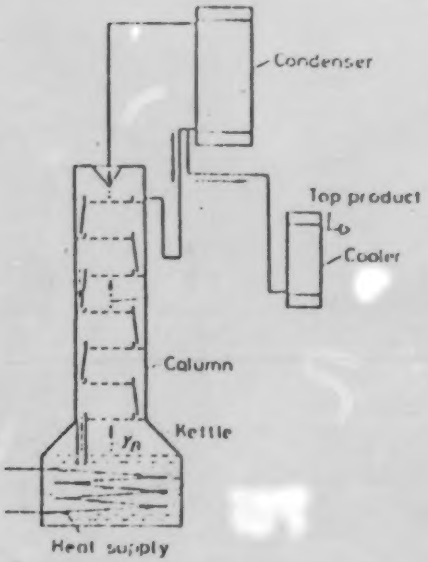

Condenser
Top product
L0
Cooler
Column
Kettle
yn
Heat supply

Fig. 5. Diagram of batch still with fractionating column
(After Billet)

manner, the ethanol content of the distillate can be held fairly constant at its initial high level until most of the ethanol is removed from the initial charge.

There are so many operating variables, design variables, variables in the water-ethanol system, and interactions between variables that it is difficult to evaluate the efficiency of a distillation set-up. Each has its own personality. Each set-up should be monitored closely under a different set of operating conditions, and the best operating time and rate selected on this basis.

D. Continuous Distillation

Continuous distillation is a system used in distilling large amounts of beer by feeding a smaller quantity at a constant rate into the system. As shown schematically in Figures 6 and 7, the system consists of the following:

1. A reboiler for heat input.
2. A stripper section or column.
3. A rectifier section or column.
4. One or more condensers and or heat removers.
5. Storage tanks for the distilled product.

Depending on layout space or preference, the rectifying section may be above the stripper section in one column as in Figure 6, or the columns may be side by side as in Figure 7.

In operation, the stripper is fed continuously with the water-ethanol mixture to be worked, preferably preheated by the hot stillage coming from the bottom of the stripper column--the hotter the better. The reboiler generates vapor or steam which passes counter to the feed and any reflux liquid which reaches the stripper. In the resulting interchange the more volatile ethanol is stripped from the downcoming reflux which is high in ethanol. The enrichment of the vapors continue with the upward movement to a maximum at the top of the column. The vapor then passes into a condenser where heat is removed and the vapor then condenses to a liquid. Part of this is refluxed and the remainder is further cooled and stored, or prepared for dehydration.

1. Internal Make-up of Columns

As stated earlier, plates (trays) or packing are used in the internal design of the still columns to provide the intimate contacts between vapor and liquid at different levels or temperatures so that equilibrium conditions are approached.

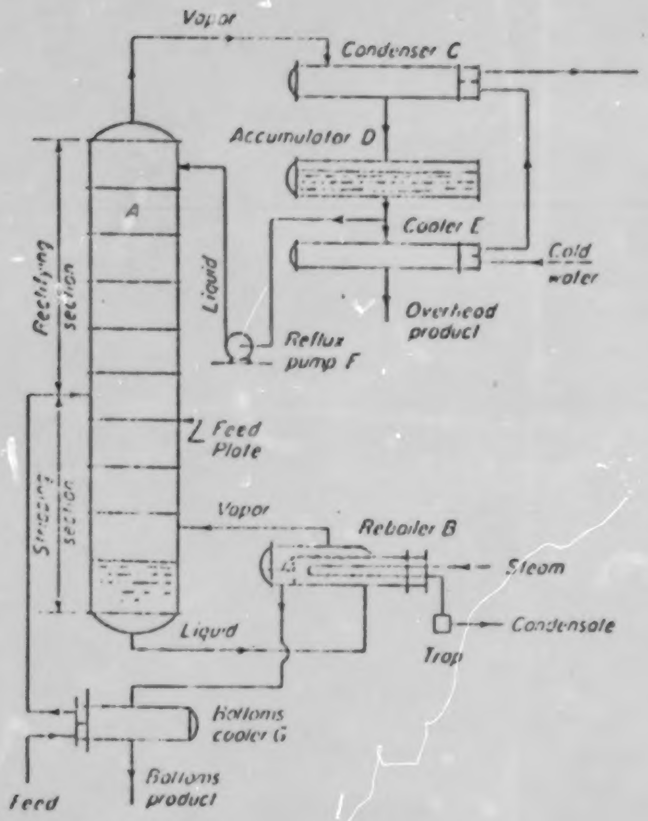
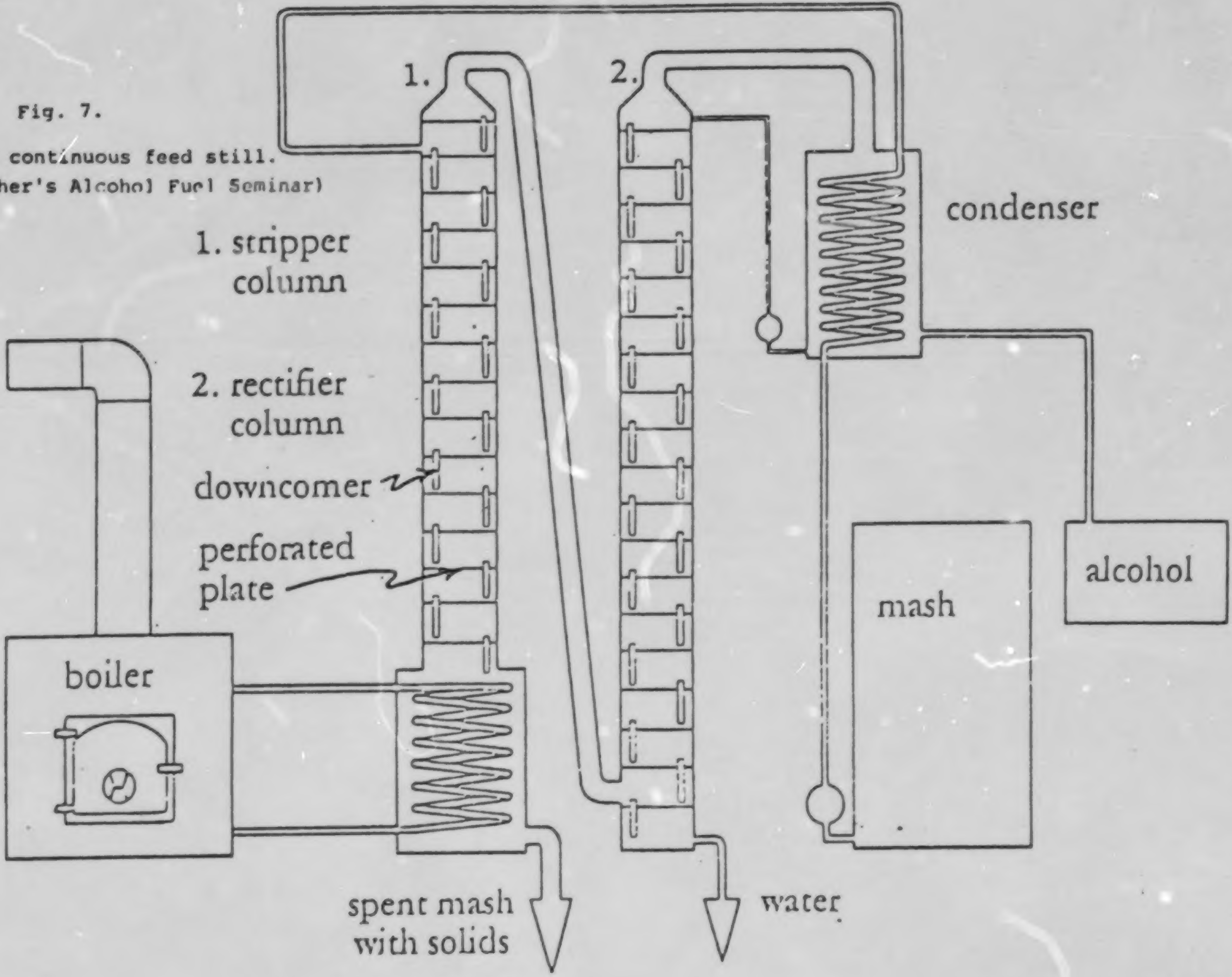

Vapor
Condenser C
Accumulator D
A
Cooler E
Cold water
Liquid
Rectifying section
Overhead product
Reflux pump F
Feed Plate
Stripping section
Vapor
Reboiler B
Steam
Condensate
Trap
Liquid
Bottoms cooler G
Bottoms product
Feed

Fig. 6. Continuous fractionating column with stacked rectifying and stripping sections. (After McCabe and Smith)

Fig. 7.

Two column continuous feed still.
(After Mother's Alcohol Fuel Seminar)


1.
2.
1. stripper column
2. rectifier column
downcomer
perforated plate
boiler
condenser
alcohol
mash
spent mash with solids
water

Plates come in many different designs varying from simple to complex depending on the type of service required. Perforated plates are simplest to construct and use, Figure 8. Perforation can vary from 1/8 to 1/2 inches in diameter and can be spaced from one to five diameters apart in a triangular or rectangular spacing. Downcomers are provided on each tray to conduct the flow of liquid from the trays above to the trays below. They must be of adequate liquid handling capacity for the size of the still. Downcomers may be pipes or wires, and usually alternate from one side of the column to the other to provide a cross flow of the downcoming liquid across the plate. This permits rising vapors to pass through the perforations in the plate and bubble through the layer of liquid maintained on the plate.

The operation of a plate column has certain limitations. Flooding is a condition which occurs when there is liquid backup in the downcomer to the plate above. When this happens, the column will fill with a foamy liquid and will stop working. This is caused by plugged plates, too great a pressure drop across the plates, too rapid a feed or reflux, or too high a vapor velocity.

Priming is a condition in which foam height on a plate becomes great enough to pass through the perforations and mix with the liquid on the plate above. It is difficult to determine when foaming will take place. Contaminants in the still feed may induce foaming. Priming can be controlled by a lower vapor velocity.

Dumping or excessive weeping in a perforated plate is a condition of liquid flowing through the perforations to the plate below. Weeping occurs when the pressure of the vapor beneath the plate is exceeded by the weight of the liquid on the plate. This will happen at low vapor velocities. In any case, some weeping does take place during most operations. For weeping to seriously affect operations, it must be excessive and continuous.

a. The Stripper Section

In constructing a distillation unit for an ethanol-water mixture, a decision must be made concerning the feed. Fermented mash has much solid matter in it. It can be fed to the still this way, or it can be clarified of solids. If unclarified beer is fed to the still, the performation in the plates should be at least 1/2 inch in diameter to permit the solids to pass to the bottom of the still where they are eliminated. If a clarified beer is used, plate performation may be much smaller.

Some provision should be made for cleaning the column. In addition to solids, the feed is slightly acid and contains proteins, which will gradually coat the plates and plug the perforations. Figure 9 shows plates mounted on a rack for easy removal and cleaning.

The stripper section should have at least eight plates and spacing between plates should be between 6 and 18 inches.

b. The Rectifier Section

The rectifying section will be handling only liquids from condensed vapors and vapors. Clogging problems experienced in the stripper will not be occurring in the rectifying section. If perforated plates are used, use from 24 to 40 plates spaced from 4 to 18 inches apart. Since the rectifying column does not handle liquids with high solid content and there is no protein build-up, the packed column is a simple alternative.

The packed column is easy to design, inexpensive to build, and easy to operate. It is a pipe filled with a packing material which will leave from 50% to 90% vapor space. Commercial packings are designed for these columns to provide maximum surface area for fluid vapor contact and shaped to provide maximum free vapor space. Figures 10 through 13 illustrate some of the commercial packings available.

For small stills, glass beads or marbles may be used. These should be at least 1/4 inch in diameter or better. The disadvantage here is the free vapor space which would run from 30% to 40%. However, this can be overcome by using a column with a larger diameter.

Other packing materials such as copper, brass, or stainless steel wool may be used. Ceramic materials and non-corrosive metals are best-suited for these purposes.

2. Heat

a. Requirements

Heat is a form of energy, just as electricity or light or moving water. It flows "downhill" from higher temperature zones to lower temperature zones at rates governed by the temperature difference and the nature of material through which it passes. As such, heat is a physical phenomenom which is measurable.

The unit of measure used in most American technology for the measurement of heat is the British Thermal Unit (Btu). This is the amount of heat necessary to raise one pound of water one degree Fahrenheit.

In the process of evaporating a liquid or liquid mixture, two stages of heating are involved.

(1) The application of heat to raise the mixture from its ambient temperature to its bubble point temperature.

(2) The application of heat to convert the mixture at its bubble point from a liquid to a vapor.

In the first case, mixture being heated is mostly water, so it can be assumed that for each gallon of beer (slightly less than 8.33 pounds per gallon), about 8.33 Btu will be required to raise the temperature one degree Fahrenheit.

EXAMPLE: Assume 100 gallons of beer at 80°F, which must be heated to a bubble point of 180°F.

180-80 = 100° the mixture must be raised.

Total heat input to raise 100 gallons of beer from 80°F to 180° would be:

100 Gallons x 8.33 Pounds/Gallon x 100 Degrees x 1 Btu/Pound/Degree = 83,300 Btu

If this is a daily rate this would be 83,300 Btu/day; if an hourly rate it would be 83,300 Btu/hour.

The second case involves the amount of heat to vaporize the distillate. This would be the same amount of heat that the condenser must remove from the vapor to condense it to a liquid. It takes 2417 Btu to evaporate one gallon of 100% pure ethanol at its bubble point temperature. For each volume percent less due to the presence of water 57 more Btu are required. Referring to the problem, using 188 proof or 94% by volume distillate, the minimum number of Btu necessary to evaporate this quantity of distillate would be:

2417 + (100-94) x 57 = 2759 Btu per gallon

In this problem, 9.89 gallons of distillate was produced. However, since some of the condensed liquid was refluxed back down the rectifying column, this liquid was evaporated again, thus requiring more heat to do so, which also means more heat in terms of Btu to be taken away in the condenser in order to condense the vapors back to a liquid.

Therefore, in order to get 9.89 gallons of 188 proof alcohol distillate assume that the reflux ratio was 4/1. This means that for every five gallons of distillate condensed four were poured back into the still. Enough heat was then input to evaporate.

(4+1) x 9.89 gallons = 49.45 gallons

The total Btu for evaporation alone would be:

49.45 gallons x 2759 Btu per gallon = 136,433 Btu.

Then the minimum total heat (disregarding any heat losses which do occur) for this distillation process would be:

Minimum total heat = heat input to bring feed to bubble point + heat input to evaporate the distillate condensed by condenser.

83,300 + 136,433 = 219,733 Btu

b. Conservation

Heat requirements can be reduced by using some of the heat given off by the still through the condenser or drained bottoms to preheat the feed. A reduction in the reflux ratio also reduces the heat requirement since less reflux has to be revaporized. Care must be taken in the reduction of this ratio so that the quality or the quantity of the overhead product is not affected.

Insulation can help reduce heat loss. By placing the rectifier directly over the stripper column, the heat loss will be less than by placing the two columns side by side and connecting them with a vapor line.

c. Application

Heat may be transferred into the still through heated metal surfaces into the liquid to be vaporized, or by steam injected into the bottom of the still. In the simple pot still, heat is applied directly to the kettle. In other more sophisticated systems the liquid to be vaporized is heated through pipes or coils. The source of heat in these coils may be hot fluids, gases, or steam. In either of these cases the efficiency of the heating device depends on the area of contact between the heated metal and liquid to be heated, and the temperature difference between the heat source and the liquid to be heated.

One of the most efficient ways of transferring heat into the still is by the injection of steam. As the steam condenses in the still it releases its heat. One cubic foot of water evaporated into steam at 212°F becomes roughly 1600 cubic feet. One pound of steam at normal atmospheric pressure occupies 26.82 cubic feet of space. This pound of steam upon condensing to water at 212° will give off 970 Btu of heat.

At 40 pounds gauge pressure in a boiler, the steam temperature would be about 286°F. One pound of this steam would release approximately 995 Btu per pound by the time it condensed and cooled to 212°F.

In this continuing problem, which has a minimum heat requirement of 219,733 Btu, the minimum steam requirement for steam at 40 pounds gauge pressure would be:

Pounds of steam = 219,733/995 = 221 pounds.

The American Society of Mechanical Engineers defines the boiler horsepower as the equivalent evaporation of 34.5 pounds of water from and at 212° per hour. This is 33,475 Btu per hour. In the Btu requirement in the problem above:

$$\text{Min Boiler Horsepower} = \frac{219{,}733}{34{,}479} = 6.3 \text{ H.P.}$$

Please bear in mind that the heat requirements discussed above are minimum theoretical requirements. Practical applications will be above these figures, depending on the efficiency of the operation.

One point worth mentioning is that the use of steam injection as a source of heat will increase the amount of water in the stillage.

III. Sizing the Still

A. General

In building a still, one always asks, "What size still must I build to produce a certain amount of ethanol?" To give a precise answer presents a complex engineering problem. There are at least 23 definable variables, plus others not definable in simple terms--plus undoubted interactions between variables, which must be taken into account in analyzing a particular design.

Basically, in choosing a column diameter several factors to consider are:

1. Temperature

2. Pressure

3. Vapor load

4. Vapor velocity

The temperature of operation of the column will be somewhere between 212°F at the bottom (boiling or bubble point of water) and 176° (the boiling or bubble point of pure ethanol) at the top where vapors are coming off. This is a temperature range of about 40°. In actual practice the feed, depending on its ethanol content, will have a bubble point somewhat less than 212°F and the distillate, depending on its water content, will have a bubble point (or dew point) below 176°F so that the actual temperature range of the column from bottom of the stripper section to top of the rectifier section will be less than 40°. With this in mind, remember the average temperature of operation of the still should be between the bubble point temperature of the feed and the bubble point (dew-point) temperature of the distillate.

Pressure in the still is higher at the bottom than at the top. Thus, the vapor generated tends to flow upward in the direction of less pressure. The internal equipment in the column will determine the pressure differential between top and bottom. For instance, a plate with small and few holes will allow only a limited amount of vapor through per unit time; thus, as in a pressure cooker, the pressure will rise beneath the plate.

In most cases, the average pressure in the still can be considered to be atmospheric since there is very little difference between top and bottom. The top is at atmospheric pressure. Standard atmospheric pressure is 14.7 pounds per square inch.

One gallon of water at 212° and standard atmospheric pressure will generate about 227 cubic feet of vapor. One gallon of pure ethanol at 176°F and standard atmospheric pressure will generate about 66 cubic feet of vapor.

In the original problem, 188-proof (94% by volume) ethanol was produced. The amount of vapor per gallon of this grade ethanol would be:

$$\frac{(94 \times 66) + (100 - 94) \times 227}{100} = 75.66 \text{ cubic feet}$$

Thus, 9.89 gallons per hour of such distillate produced with a 4/1 reflux ratio requires:

(4 + 1) x 9.89 = 49.45 gallons per hour through the still.

49.45 x 76.66 = 2741 cubic feet/hour.

Cubic feet per second would be: 3741/3600 = 1.04 cubic feet/second.

Assuming a vapor rate of flow of 3 feet per second in the space between the plates, the cross sectional area required would be:

$$1.04/3 = .35 \text{ square feet}$$

In terms of diameter, this would be from the formula for the area of a circle.

$$A = \frac{\pi d^2}{4}$$

$$.35 = \frac{\pi d^2}{4}$$

Solving for column diameter

$$d = \sqrt{\frac{.35 \times 4}{\pi} = .67 \text{ feet}}$$

$$.67 \text{ feet} \times 12''/\text{feet} = 8.04 \text{ inches}$$

To be safe, the choice should be the next higher size in the material you are using.

B. Column Height

If the recommended 8 plates in the stripper section--spaced 10 inches apart--were used, then there would be 80 inches (about 7 feet) of stripper section. If the maximum of 40 plates were used in the rectifier section--with 6-inch spacing--an additional 20 feet of column would be required. This 20 feet, plus the approximately 7 feet for the stripper section, would give a total of 27 feet. Larger spacings would thus require taller columns.

1. Packed Column Design

It is more economical and practical if the diameter of packed columns does not exceed 15 or 20 inches. If columns are less, they are difficult to fit with trays, and costly to manufacture. An exact computation for packed column design on theoretical grounds is not feasible because of the complexity of flow patterns which may develop. The main irregularities of flow are the channeling of down-flowing liquid into rivulets, and the blow-by of upward flowing vapors. These usually increase with greater packing depth. Some of the blow-by caused by the orientation along the column wall of the packing elements, which have been dumped randomly into the column, can be avoided by choosing an element size whose diameter is one tenth the shell diameter.

Another requirement for good separation is uniform liquid distribution of the reflux at the column head. A device constructed of perforated cross pipes, with reach large enough to spread the liquid over the entire cross section of the column at the top of the packing, should be used (Figure 14).

A good packing element must prevent any segregation of liquid away from the vapor and must promote as much mixing of liquid and vapor as possible.

A simple but efficient packing element in the shape of a Rashig Ring can be cut from tubular stock. If the length is uniform and is about equal to the diameter, the amount of free space through which vapors and liquids can pass through will be about 75%.

Again, for the previously assumed vapor rate of 3 feet per second for the cross section in an uncluttered column, the amount was .35 square feet. However, since in a packed column the flow area is less, using either homemade or commercial type Rashig Rings, the overall area of the column necessary to create .35 square feet of flow area would be:

$$\frac{.35}{.75} = .47 \text{ square feet}$$

This means a column diameter in feet of:

$$d = \sqrt{\frac{.47 \times 4}{\pi}} = .77 \text{ feet}$$

In inches, this would be: .77 x 12 = 9.28 inches.

A nine-inch column or greater would be suitable.

A ratio of 10/1 is recommended for packing element diameter. Tubing stock closest in diameter to one tenth of the column diameter should be chosen for the homemade Rashig Rings.

Packing effectiveness can be related in the depth or height of packing necessary to equal a theoretical plate. This paper has derived a very approximate relationship based on the diameter (d) in inches of the packing element. THIS IS:

Packing depth in inches = 13 x d.

Assuming an element whose diameter is one inch or slightly less a packing depth of approximately one foot would be required for each theoretical plate. Various sources indicate theoretical plate requirements from 15 to 40. Assuming 15 as a minimum, the total packing height should not be less than 15 feet.

However, it is possible to use a greater height and this may be necessary for certain designs. As the packed distance through which the vapors travel increase so must the pressure increase at the bottom of the column in order to maintain the desired rate of vapor flow.

Allowing two feet at the top for a vapor collection chamber and a reflux distributor, and two feet at the bottom for a vapor chamber, the total length of the rectifying column would be about 19 feet.

Provisions should be made for adding on more column and packing or reducing the packed height if operating results dictate.

2. Packing Support Grid

A plate or grid support structure should be bolted, welded, or flanged into the column where the bottom of the packing will rest to support the packing load. The only requirements are that it must be strong enough to support the weight of the packing above, that it provide as great or greater percent of vacant space for vapor and liquid passage as the packing, and that it provide for equal distribution of rising vapors to all parts of the bottom surface of the packing.

C. Materials

The nature of the materials handled and the conditions of temperature and pressure under which they are handled would determine the types of material best suited for use in the system. The beer or fermentation product which is fed to the still is basically a slightly acid water-ethanol mixture that ranges from 8% to 12% ethanol by volume. It may contain minor amounts of amyl alcohols, proteinaceous matter, and other additions in solution that was added during the fermentation process. In addition, solids remaining from the fermentation process may be included.

The temperature of the still and its contents will vary between 212°F and 173°C. Pressures will vary from atmospheric at the top to slightly more than atmospheric at the bottom, depending on the flow resistance the vapor meets on its upward path to the condenser.

These factors constitute the environment within the still. The warm temperatures and acidic nature of the feed is conducive to corrosion or rusting. To reduce maintenance problems and to extend the life of the equipment, all parts in contact with the feed and stillage should be of non-corrosive materials, such as stainless steel or copper. This material is expensive to use and the average backyard still-maker will probably choose cheaper steel, ceramic, or plastic, or a combination of these.

Mild steels are more susceptible to corrosion than the tougher and harder steels used for certain industrial purposes. Mild steel piping is cheaper and more readily available.

Ceramics include a wide variety of substances, e.g., glass, brick, stone, concrete, or porcelain enamels. Most ceramic materials are chemically inert and therefore will not corrode. It is possible that some of these materials can be ingeniously applied in backyard still construction. Ceramic packing elements are commercially available for packed columns. Large diameter glass tubing is available from chemical supply houses.

Plastics offer interesting possibilities of application. The more rigid thermoset plastics offer the most resistance to the temperatures encountered in the ethanol distillation process. Tefzel (e.g. Teflon) and high-density polyethylene hold up best over a period of time against temperature and reaction with ethanol. Polypropylene, polymethylpentene, polycarbonate, and the very common polyvinylchloride may hold up as well as the first group named, depending on severity of usage.

Most plastics have the property of softening when heated. Application of direct heat will result in charring and complete destruction. It would probably be best to stay away from plastics on the feed and stripper side of the still. Temperatures are lower on the distillate and rectifier side, and some plastics probably could be used there.

ALCOHOL FUEL PRODUCTION

MODULE V - AGRICULTURAL PRODUCTION OF ALCOHOL FUEL

I. Introduction:

Students of Alcohol Fuel Production may have gained expertise in many areas, and yet not have the full concept until they have dealt with producing and using ethanol on a day-to-day basis. The purpose of this module is to teach a student the basic procedures that must be routinely followed in order to produce alcohol fuel, and to supply the necessary information needed in order to put that fuel to work. Therefore, this module is designed to be accompanied with actual hands-on laboratory work with an ethanol plant.

The size and scope of the plant is not of significant importance because almost all concepts involved are the same with respect to technology. The size of the unit does not alter the basic concepts to be taught. Thus, a chemistry lab will suffice if a larger plant is not available.

Information about how alcohol fuel is to be used is also included. Basic knowledge of ethanol as a fuel is taught along with the procedures to follow that will allow its use as a substitute for most conventional fossil fuels.

II. Objectives:

Upon completion of this module the student will be able to:

A. Identify terms and definitions related to agricultural production of alcohol fuel.

B. Point out the basic procedures involved in ethanol production, including flow of materials, feedstock preparation, fermentation, distillation, and drying.

C. Cite the government regulation which controls denaturing of fuel ethanol.

D. Give examples of ways to store ethanol as it is produced.

E. List the types and uses of stillage that can be produced.

F. Summarize the processes involved in culturing of enzymes and yeast.

G. Explain routine maintenance and repairs required in ethanol production.

H. Describe hazards associated with ethanol production; list ways to prevent fire and explosion hazards; identify properties of cleaning solvents and toxic materials; explain how to handle acids and bases, how to prevent burns, and how to safely accomplish maintenance.

I. Quote government booking requirements in regard to the ethanol produced.

J. Summarize the use of ethanol as a fuel for internal combustion engines.

K. Point out alternative uses for ethanol other than for trucks, automobiles, and tractors.

III. Instructional Materials:

The following items are needed to aid with the instruction of this module:

A. Laboratory materials: Chemistry distillation apparatus, hot plate, stirring rods, thermometers, glassware (beakers and distillation apparatus), scales, parafilm, chemicals (sulfuric acid, iodine, lime), sugar test tape, litmus paper, hydrometers, goggles and lab coats.

B. Raw materials: Grain (meal form), distillers dried yeast, enzymes, penicillin, storage containers, basic mechanics tool kit, first aid kit.

C. Classroom materials: Calculator (pocket size), pens, paper, rulers, paperclips, notebooks, thermo projection transparencies.

IV. References:

A. A Guide to Commercial-Scale Ethanol Production and Financing, Solar Energy Research Institute, November 1980, SERI/SP-751-877, UC-61.

B. A Learning Guide for Alcohol Fuel Production, July 1979, Colby Community College, Colby, Kansas.

C. Alcohol Fuels - Use, Principles, and Economics, by Steven J. Winston, 1980.

D. Ethanol as a Fuel for Internal Combustion Engines - Spark Ignition and Diesel, by W. A. LePori and R. R. Davison, July 1-2, 1980, Alcohol Fuel Symposium, Texas A&M University, College Station, Texas.

E. Fuel From Farms - A Guide to Small Scale Ethanol Production, Solar Energy Research Institute, February, 1980, SERI/SP-451-519, UC-61.

F. Technical and Product Information, Biocon (U.S.) Inc., 1980.

MODULE V - AGRICULTURAL PRODUCTION OF ALCOHOL FUEL

Terms and Definitions:

1. Absolute Alcohol - Completely dehydrated ethyl alcohol of the highest proof obtainable (200°-proof) also "neat" alcohol.

2. Acid Hydrolysis - Decomposition or alteration of a chemical substance by water in the presence of acid.

3. Acidity - The measure of how many hydrogen ions a solution contains per unit volume; may be expressed in terms of pH.

4. Alcohol - The family name of a group of organic chemical compounds composed of carbon, hydrogen, and oxygen; a series of molecules that vary in chain length and are composed of a hydrocarbon plus a hydroxyl group, $CH_3-(CH_2)n-OH$; includes methanol, ethanol, isopropyl alcohol, and others.

   Defined in the Crude Oil Windfall Profit Tax Act of 1980 (26 USC 44E P.L. 96-223) to include "methanol and ethanol but does not include alcohol produced from petroleum, natural gas, or coal or alcohol with a proof less than 150."

   Defined in The Energy Security Act (42 USC 8802, P.L. 96-294) as "alcohol (including methanol and ethanol) which is produced from biomass and which is suitable for use by itself or in combination with other substances as a fuel or as a substitute for petroleum or petrochemcial feed stocks."

5. Alcohol Fuel Plant - Under BATF regulations, a distilled spirits plant established solely for producing, processing, and using or distributing distilled spirits to be used extensively for fuel use.

6. Aldehydes - Any of a class of highly reactive organic chemical compounds obtained by controlled oxidation of primary alcohols, characterized by the common group CHO, and used in the manufacture of resins, dyes, and organic acids.

7. Alkali - Soluble mineral salt of a low-density, low-melting point, highly reactive metal; characteristically "basic" in nature.

8. Alpha-Amylase - Enzyme which liquefies starch by conversion to dextrins.

9. Ambient - The prevalent surrounding conditions usually expressed as functions of temperature, pressure, and humidity.

10. Amino Acids - The naturally occurring, nitrogen-containing building blocks of protein.

11. Anaerobic Digestion - A type of bacterial degradation of organic matter that occurs in the absence of air (oxygen) and produces primarily carbon dioxide and methane.

12. Anhydrous - Devoid of water; refers to a compound that does not contain water either absorbed on its surface or as water of crystallization.

13. Anhydrous Ethanol - 100-percent alcohol, neat alcohol, 200°-proof alcohol.

14. ATF - Should refer to BATF, (Bureau of Alcohol, Tobacco and Firearms) for proper usage.

15. Azeotropic Distillation - Distillation in which a substance is added to the mixture to be separated in order to form an azeotropic mixture with one or more of the components of the original mixture; the azeotrope formed will have a boiling point different from the boiling point of the original mixture and will allow separation to occur.

16. Basic Hydrolysis - Decomposition or alteration of a chemical substance by water in the presence of alkali.

17. Batch Fermentation - Fermentation of a specific quantity of material conducted from start to finish in a single vessel.

18. Biomass - Organic matter, such as trees, crops, manure, and aquatic plants, that is available on a renewable basis.

19. Boiling Point - The temperature at which the transition from the liquid to the gaseous phase occurs in a pure substance at fixed pressure.

20. British Thermal Unit - (Btu) - The amount of heat required to raise the temperature of one pound of water one degree Fahrenheit under stated conditions of pressure and temperature (equal to 252 calories, 778 foot-pounds, 1055 joules, and 0.293 watt-hours); it is a standard unit for measuring quantity of heat energy.

21. Calorie - The amount of heat required to raise the temperature of one gram of water one degree Centigrade.

22. Carbohydrate - A chemical term describing certain neutral compounds made up of carbon, hydrogen, and oxygen; includes all starches and sugars; a general formula is $C_x(H_2O)y$.

23. Catalysis - The effect produced by a small quantity of a substance (catalyst) on a chemical reaction, after which the substance (catalyst) appears unchanged.

24. Cellulase - An enzyme capable of decomposing cellulose into simpler carbohydrates.

25. Cellulose - The main polysaccharide in living plants, forms the skeletal structure of the plant cell wall; can be hydrolyzed to glucose.

26. Celsius - (Centigrade): A temperature scale commonly used in the sciences; at sea level, water freezes at 0°C and boils at 100°C. $C^o = 5/9(F-32)$.

27. Completely Denatured Alcohol (CDA): Ethyl alcohol which is at least 160° proof blended, pursuant to formulas prescribed by BATF, with sufficient quantities of various denaturants to make it unfit for and not readily recoverable for beverage use; this may then be distributed through retail outlets without permits.

28. Continuous Fermentation - A steady-state fermentation system that operates without interruption; each stage of fermentation occurs in a separate section of the fermenter, and flow rates are set to correspond with required residence times.

29. Dehydration - The process of removing water from any substance by exposure to high temperature or by chemical means.

30. Denaturant - A substance added to ethanol to make it unfit for human consumption so that it is not subject to alcohol beverage taxes.

31. Enzymes - The group of catalytic proteins that are produced by living microorganisms; enzymes mediate and promote the chemical processes of life without themselves being altered or destroyed.

32. Ethanol - Chemical formula C_2H_5OH; the alcohol product of fermentation that is used in alcoholic beverages and for industrial purposes; blended with gasoline to make gasohol; also known as ethyl alcohol or grain alcohol.

33. Ethyl Alcohol - See Ethanol.

34. Evaporation - Conversion of a liquid to the vapor state by the addition of latent heat of vaporization; usually refers to vaporization into the atmosphere.

35. Facultative (Anaerobe) - A microorganism that grows equally well under aerobic and anaerobic conditions.

36. Feedstock - The base raw material that is the source of sugar for fermentation.

37. Fermentable Sugar - Sugar (usually glucose) derived from starch or cellulose that can be converted to ethanol (also known as reducing sugar or mono-saccharide).

38. Fermentation - A microorganically mediated enzymatic transformation of organic substances, especially carbohydrates, generally accompanied by the evolution of a gas; the conversion of simple sugars to ethanol with the aid of enzymes.

39. Fermentation Ethanol - Ethyl alcohol produced from the enzymatic transformation of organic substances.

40. Fossil Fuel - Any naturally occurring fuel of an organic nature which originated in a past geologic age (such as coal, crude oil, or natural gas).

41. Fractional Distillation - A process of separating alcohol and water (or other mixtures) by boiling and drawing off vapors from different levels of the distilling column.

42. Fructose - A fermentable monosaccharide (simple) sugar of chemical formula $C_6H_{12}O_6$; fructose is a ketohexose.

43. Fuel Grade Alcohol - Usually refers to ethanol of 160° to 200° proof, although 100° to 200° proof can be used with diesel fuel.

44. Gasohol (Gasahol) - A registered trademark held by the State of Nebraska for a fuel mixture of agriculturally derived 10 percent anhydrous fermentation ethanol and 90 percent unleaded gasoline; it is often incorrectly used to mean any mixture of alcohol and gasoline to be used for motor fuel.

45. Gasoline - A volatile, flammable liquid obtained from petroleum that has a boiling range of approximately 200° to 216° C and is used as fuel for spark-ignition internal combustion engines.

46. Gelatinization - The rupture of starch granules by heat to form a gel of soluble starch and dextrins.

47. Glucose - A monosaccharide; occurs free or combined and is the most common sugar; chemical formula $C_6H_{12}O_6$; glucose is an aldohexose.

48. Heat of Condensation - The same as the heat of vaporization, except that the heat is given up as the vapor condenses to a liquid at its boiling point.

49. Hydrolysis - The decomposition or alteration of a substance by chemically adding a water molecule to the unit at the point of bonding.

50. Hydrometer - A long-stemmed glass tube with a weighted bottom; it floats at different levels depending on the relative weight (specific gravity) of the liquid; the specific gravity or other information is read where the calibrated stem emerges from the liquid.

51. Inulin - A polymeric carbohydrate comprised of fructose monomers found in the roots of many plants, particularly Jerusalem artichokes.

52. Lactic Acid - $C_6H_6O_3$, the acid formed from milk sugar (lactose) and produced as a result of fermentation of carbohydrates by bacteria called Lacto-bacillus.

53. Lactose - A crystalline disaccharide made from whey and used in pharmaceuticals, infant foods, bakery products, and confections; also called "milk sugar", $C_{12}H_{22}O_{11}$.

54. LHV - Lower heating value; the heat released during combustion of fuel if all products are cooled to room temperature while water remains as steam; the lower heating value is more representative of typical fuel burning than HHV.

55. Liquefaction - The change in the phase of a substance to the liquid state; in the case of fermentation, the conversion of water-insoluble carbohydrate to water-soluble carbohydrate.

56. Malt - Barley softened by steeping in water, allowed to germinate, and used especially in brewing and distilling as a source of amylase.

57. Maltose - A disaccharide of glucose.

58. Mash - A mixture of grain and other ingredients with water to prepare wort for brewing operations.

59. Meal - A granular substance produced by grinding.

60. Membrane - A sheet polymer which separates components of solutions by permitting passage of certain substances but preventing passage of others.

61. Methanol - A light volatile, flammable, poisonous, liquid alcohol, formed in the destructive distillation of wood or made synthetically and used especially as a fuel, a solvent, an antifreeze, or a denaturant for ethyl alcohol, and in the synthesis of other chemicals; methanol can be used as fuel for motor vehicles; also known as methyl alcohol or wood alcohol.

62. Methyl Alcohol - Also known as methanol or wood alcohol.

63. Molecular Sieve - A compound which separates molecules by selective penetration into the sieve space on the basis of size, charge or both.

64. Molecule - The chemical term for the smallest particle of matter that is the same chemically as the whole mass.

65. Monomer - A simple molecule which is capacle of combining with a number of like or unlike molecules to form a polymer.

66. Osmotic Pressure - Applied pressure required to prevent passage of a solvent across a membrane which separates solutions of different concentration.

67. Packed Distillation Column - A column or tube constructed with a packing of ceramics, steel, copper, or fiberglass-type material to increase surface area through which vapors or liquid may pass.

68. pH - A term used to describe the free hydrogen ion concentration of a system; a solution of pH less than 7 is acid; pH of 7 is neutral; pH over 7 is alkaline.

69. Polymer - A substance made of molecules comprised of long chains or cross-linked simple molecules.

70. Pounds Per Square Inch Absolute - (psia) - The measurement of pressure referred to a complete vacuum or 0 pressure.

71. Proof - A measurement of the alcohol concentration in an alcohol-water mixture, equal to twice the percentage by volume of the alcohol; e.g., 80-percent alcohol equals 160° proof, 100-percent alcohol equals 200° proof.

72. Proof Gallon - A U.S. gallon of liquid which is 50-percent ethyl alcohol by volume or the alcohol equivalent thereof; also one tax gallon.

73. Protein - Any of a class of high-molecular-weight polymer compounds comprised of a variety of amino acids joined by peptide linkages.

74. Pure Ethyl Alcohol - Ethyl alcohol that has not been denatured and is usually sold as 190° proof and 200° proof (absolute).

75. Saccharide - A simple sugar or a compound that can be hydrolyzed to simple sugar units.

76. Saccharify - To hydrolyze a complex carbohydrate into simpler soluble fermentable sugars, such as glucose.

77. Saccharomyces - A class of single-cell yeasts which selectively consume simple sugars.

78. Set Back - The liquid portion of the stillage that is recycled as a portion of the process liquid in the mash preparation.

79. Settling Time - In a controlled system, the time required for entrained or colloidal material to separate from the liquid.

80. Sight Gauge - A clear calibrated cylinder through which liquid level can be observed and measured.

81. Simple Sugars - See Fermentable Sugars.

82. Small-Scale Biomass Energy Project - Defined in the Energy Security Act (42 USC 8802, P.L. 96-294) as "a biomass energy project with an anticipated annual production capacity of not more than 1,000,000 gallons of ethanol per year, or its energy equivalent of other forms of biomass energy."

83. Special Fuel - Defined in the Crude Oil Windfall Profit Tax Act of 1980 (26 USC 44E, P.L. 96-223) as "any liquid fuel (other than gasoline) which is suitable for use in an internal combustion engine.

84. Specially Denatured Alcohol (SDA) - Ethyl alcohol to which sufficient quantities of various denaturants have been added, pursuant to formulas prescribed by Federal regulations, to render it unfit for beverage purposes; specially denatured alcohol may be distributed only to persons holding BATF permits.

85. Specific Gravity - The ratio of the mass of a solid or liquid to the mass of an equal volume of distilled water at 4° C.

86. Spent Grains - The nonfermentable solids remaining after fermentation of a grain mash.

87. Starch - A carbohydrate polymer comprised of glucose monomers linked together by a glycosidic bond and organized in repeating units; starch is found in most plants and is a principal energy storage product of photo synthesis; starch hydrolyzes to several forms of dextrin and glucose.

88. Still - An apparatus for distilling liquids, particularly alcohols; it consists of a vessel in which the liquid is vaproized by heat, and a cooling device in which the vapor is condensed.

89. Stillage - The nonfermentable residue from the fermentation of a mash to produce alcohol.

90. Stoichiometric Ratio - The ratio of chemical substances necessary for a reaction to occur completely.

91. Sucrose - A crystalline disaccharide carbohydrate found in many plants, mainly sugar cane, sugar beets, and maple trees; $C_{12}H_{22}O_{11}$.

92. Surfactant - Surface-active agent, a substance that alters the properties, especially the surface tension, at the point of contact between phases; e.g., detergents and wetting agents are typical surfactants.

93. Tetraethyllead (TEL) - An octane enhancer for gasoline now under environmental restriction.

94. Thermal Efficiency - Energy heating value; the ratio of energy output to energy input.

95. Thermophilic - Capable of growing and surviving at high temperatures.

96. Thin Stillage - The water-soluble fraction of a fermented mash plus the mashing water.

97. Tray - One of several types of horizontal pieces in a distillation column.

98. Vacuum Distillation - The separation of two or more liquids under reduced vapor pressure; reduces the boiling points of the liquids being separated.

99. Vaporize - To change from a liquid or a solid to a vapor, as in heating water to steam.

100. Vapor Pressure - The pressure at any given temperature of a vapor in equilibrium with its liquid or solid form.

101. Wet Milling - A process similar to dry milling except that the various components of grain are separated in water.

102. Whole Stillage - The undried "bottoms" from the beer well comprised of nonfermentable solids, distillers solubles, and the mashing water.

103. Wort - The liquid remaining from a brewing mash preparation following the filtration of fermentable beer.

104. Yeast - Single-cell microorganisms (fungi) that produce alcohol and CO_2 under anaerobic conditions and acetic acid and CO_2 under aerobic conditions; the microorganism that is capable of changing sugar to alcohol by fermentation.

MODULE V - AGRICULTURAL PRODUCTION OF ALCOHOL FUEL

OUTLINE

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ALCOHOL FUEL PRODUCTION

MODULE V - AGRICULTURAL PRODUCTION OF ALCOHOL FUEL

I. Production of Ethanol Fuel

The purpose of this module is to discuss all of the basic procedures which must be routinely followed to produce ethanol on a regular basis.

A. Basic Preparations

There must be a balance of the flow of material into a facility that produces ethanol and the material that flows out. Ethanol cannot be produced without the proper raw materials, and it must also be in unison with each of the streams of end products exiting the plant. The following are most of the major considerations that must be dealt with in an organized procedure of operation.

1. Feedstocks

The ethanol production facility should have at least a moderate capability for on-site storage of feedstocks. This can range from two days to two weeks of plant capacity. Feedstock must be received at a rate appropriate to maintain on-site supplies to allow for uninterrupted production.

Feedstock receipts are generally accepted on a weight basis. Since deliveries are most commonly made in truck-size lots, it is necessary to have access to a truck scale. Often local feed companies and/or elevator operators provide truck-weighing service for a minimal fee. A larger-scale ethanol production business may be able to directly justify the expense of purchasing and installing a truck scale.

All feedstock receipts should note the actual weight of feedstock delivered, the amount of moisture contained, and an analysis of protein and carbohydrate. When purchasing feedstock, preference should be given to feedstock that is relatively low in moisture and high in carbohydrate. In contrast to animal feeding, high protein feedstocks produce a lower yield of ethanol than those high in carbohydrate.

Time should be allowed within the operator's daily routing for receipt of feedstock, especially if mechanical or automatic unloading equipment is not available. If grain feedstock is delivered in grain trucks with dump boxes, the receiving area must be equipped to allow convenient transfer to the storage area. This can be done with below-grade bunkers or bins (be wary of moisture collecting in these) with augers and elevators, or by piling on clean floors inside grain bins.

2. Receipt of Chemicals and Supplies

The rate at which acids, bases, antiseptics, and other chemicals are consumed is dependent upon the care with which the plant is operated. An operator who makes pH adjustments without bothering to calculate the appropriate amount of acid or base to add will invariably use more of both than is necessary. A facility that is not kept clean and properly washed down will require much more use of antiseptics to control microbial contaminants than one that is.

Chemical purchases should be planned on the basis of existing inventories, shelf life, the rate of consumption, and the normal lead time for delivery. Receipts should indicate the concentration of the chemicals and the weight delivered. All chemicals should be moved directly from the receiving area to the appropriate storage area to prevent possible damage to containers and any hazardous spills. Some chemicals may also require temperature control and necessitate refrigeration.

3. Receipt of Fuel

Production facilities which operate on electricity, natural gas, or other pipeline fuel receive their fuel continuously as it is needed. All receipts are metered and recorded. Facilities that require other fuels, particularly those that operate on solid fuels, such as coal, wood, or agricultural residue, depend on maintaining sufficient on-site reserves to operate the plant for a given period of time. The size of the on-site reserves usually reflects the availability of the fuel and the relative reliability and frequency of deliveries. Plants which operate during the winter months in cold climates usually increase onsite stockpiles of fuel during this period because more fuel is needed, and the potential for winter storms that paralyze transportation is high.

Fuel receipts should indicate the weight of fuel delivered, its moisture content (if solid), some indication of its caloric value, and an indication of its bulk density. To the extent possible, payment should be based on the caloric value of the fuel, not on the weight alone.

Fuel should be stored in a manner that keeps it readily accessible in all conceivable situations but isolated from potential ignition sources. If feasible, fuel should be protected from moisture and stored above flood plane and ground water.

4. Receipt of Denaturant

The Bureau of Alcohol, Tobacco, and Firearms has approved the use of gasoline as a denaturant for anhydrous fuel ethanol.

Thus, it is possible to do on-site blending of anhydrous ethanol and gasoline to produce simultaneously denatured ethanol and blended internal combustion engine fuel. Because the BATF requires adherence to specific denaturing formulas, the quantities of ethanol and gasoline must be carefully measured and appropriate records must be maintained. Thus, a tank for receiving and storing denaturant is advisable, and a means for accurately approximating the volume contained at any level is desirable. In this fashion, record-keeping can be greatly simplified. Orders for denaturant should be placed as inventories are consumed, allowing for appropriate delivery lead time. Denaturants of other types and formula, such as Isobutyl Ketone, are acceptable and may be preferred if shipping wet alcohol to another site for drying.

5. Receipt of Yeast and Enzymes

Both the yeast and the saccharifying enzymes can be cultured as part of plant operations. If this is done, time must be allocated in the operator's routine to accomplish all of the tasks necessary to do this. (Section V describes these procedures in more detail).

If enzymes are purchased, orders must be placed according to the rate of consumption and available inventories. Since enzymes are generally purchased from large commercial suppliers which in most cases are not locally situated, the lead time for delivery is quite significant. In all cases, the manufacturer's recommended use rates should be followed. They know their enzymes best, and the best results can be expected following their instructions. Reductions of enzyme proportions to conserve enzymes usually result in either slower conversion of starch to sugar or reduced conversion efficiency. Either result effectively reduces the plant capacity.

With the exception of very small-scale systems, most ethanol production facilities must produce their own yeast to be economically competitive. Nonetheless, periodic purchase of fresh yeast strains to maintain yeast quality is a common practice. Unless the facility can afford the services of a microbiologist to assure that yeast cultivation practices are producing a consistently pure culture, such strain purification is advisable. Yeast orders should be of sufficient size to permit rapid propagation of pure culture. The appropriate media for culturing yeast should be maintained in inventory. Orders should be placed according to rates of consumption and delivery lead times.

6. Shipping Ethanol

The distribution of product is the payoff of a process. It can also be the bottleneck that keeps a process from operating at full capacity. The Bureau of Alcohol, Tobacco, and Firearms requires that ethanol be denatured in specific volumetric proportions. Thus, shipments should be planned to fit within a regular production schedule so the appropriate quantities are available, and to assure that production does not have to be interrupted merely because product tanks are full.

All shipping records should indicate the quantity of ethanol delivered, its moisture content, the denaturation formula used, the date of transaction, and the name of the person supervising the shipment.

7. Shipping Stillage

On a volume basis, approximately nine gallons of stillage are produced for every gallon of ethanol produced. Although between 80% and 90% of this volume is water, the entire quantity must be appropriately treated for use, sale, or disposal. Distribution of stillage to the various outlets must be planned in consideration of stillage treatment capacity, on-site stillage storage capacity, and market demand. Vehicle access for loading and maneuvering in the shipping yard is especially important for stillage distribution because of the relatively large volume of production.

Stillage shipment records should indicate the weight shipped, the average protein content, and the average water content.

8. Shipping Carbon Dioxide

Carbon dioxide is a coproduct of ethanol fermentation. Recovery of carbon dioxide for soft drink production, food processing, greenhouse use, or dry ice production is justified only if a local market for these carbon dioxide products is readily available. The value of this coproduct is very site-and-demand-specific and cannot be projected on a general basis. Prices of $3 to $5/ton have been reported for uncleaned, uncompressed, raw gas. In most cases, however, no credit for this coproduct should be taken, and it is safely ventilated into the atmosphere.

B. Feedstock Preparation

Three basic categories of carbohydrate feedstocks can be used for ethanol production:

Starch Crops: Cereal grains, such as corn, milo, wheat, oats, or barley. Starchy tubers, such as white potatoes and sweet potatoes.

Sugar Crops: Sugarcane, sweet sorghum, Jerusalem artichokes, sugar beets, fruit crops, etc.

Alternatives are biomass conversion, such as municipal wastes and cellulosic conversion, such as trees, shrubs, grass, and forages.

Each requires some unique processing and handling procedures along with the steps that are common to all. In every instance, the objective is to recover and convert all of the material that can be converted to simple sugar to produce a fermentable "mash".

NOTE: See Tables 1-3

1. Milling Grains

The objectives of grain milling are:

a. To expose the inner portion of the kernel endosperm by splitting and removing the husk.

b. To crush or disintegrate the inner kernel into uniform particles that are readily accessible to enzymatic action.

c. To minimize the quantity of fines (flour) that is produced.

An ideally crushed grain would contain no uncrushed kernels, the majority of the husks split from end to end with no endosperm particles clinging to the broken husk, a uniform particle size corresponding to that caught on a 20 mesh screen, and a minimum of snowy flour. Flour tends to make dough and is difficult to work with, thus creating problems in handling and conversion.

Many types of grain grinders will serve adequately; however, feed mills will not produce the same quality for large-scale operations as will a roll mill specifically designed for preparing mashes. Small-scale operators may find it most economical to use the farm type mill, although maximum conversion may not be obtained. Stillage will be bulkier and easier to handle. It is important to recognize that clean grain leads to fewer problems throughout the fermentation than does grain containing large amounts of dirt, dust, and insect parts. An air blast cleaner is well worth its expense.

2. Washing and Mashing Tubers

By definition, tubers are harvested by digging them out of the soil. The equipment used to separate them from the dirt is generally incapable of reliably differentiating between a tuber of a given size and rocks of the same size. Although hand-sorting is often employed to reduce the number of rocks, many still slip by into stored inventories. As tubers are brought from storage to the preparation system, they should be washed and screened to remove rocks. This both protects the mashing equipment and removes unnecessary dirt from the system. Because most tubers will float and most rocks will not, a washing flume is often used to separate dirt and rocks from tubers. This flume must be periodically cleaned to remove sludge as it builds up and the recirculating water must be filtered.

Tubers can be mashed by passing them through extruders, rollers, ball mills, or hammermills. The skins, which are not fermentable, must be pulverized into small enough pieces to prevent system plugging, or removed. Skin removal can be done prior to pulverizing the tuber or after pulverizing is complete. Manual peeling is time-consuming and labor-intensive and is practical only in extremely small-scale operations. Mechanical peeling is wasteful and usually incomplete. Chemical peeling requires additional chemicals and poses potential fermentation problems (high alkalinity and high osmotic pressure). Many operations rely on mechanical peeling followed by centrifugation to remove the remaining peels after pulverization is complete. Also, although the amount of total nonfermentable material is increased by allowing the peels to remain in the mash, the potential savings in equipment and effort often justifies doing so. If this is done, all pump valves, metering devices, and even the beer still must be designed or selected according to ability to function in the presence of peels.

3. Extracting Sugars

Sugar can be extracted from the various sugar crops by mashing, pressing, leaching, or by combinations of these processes. Cane plants such as sugarcane and sweet sorghum are commonly run through a twin roll press, split, and depithed. Sugar beets can be sliced and leached or mashed in a two-roll press. The leaching process can produce a dilute sugar concentration if a high volume of liquid is used to extract the sugar. If a low volume of liquid is employed, solvent saturation can result in large quantities of sugar remaining in the pulp because the maximum sugar concentration in the solution has already been achieved.

4. Preparing a Mash

The quality of the mash dominates the quality of the fermentation. Mashes should be prepared by using high quality water low in carbonates and mineral salts. The amount of carbohydrate should be calculated to yield a mixture that has 2% of sugar by weight for every 1% of alcohol by weight in the finished beer. Thus, if a beer containing 8% ethanol by weight (about 10% by volume) is desired, the sugar concentration should be adjusted to about 15% by weight. This is done by first computing the quantity of carbohydrate in the feedstock. (The average carbohydrate content of feedstocks can be easily determined by any agricultural testing laboratory. This should be done for each distinctly separate large quantity of feedstock processed, e.g., when changing from one supplier to another.)

The efficiency of conversion of starch to simple sugars ranges from 85% to 95%, so allowances for this fact should be included in the calculations. If the fermenter volume is known, calculations for the final mash are simple.

The first rule to observe is that in closed fermentation tanks a "free board" space above the liquid at least equivalent to one-tenth of the fermenter volume is necessary to allow the CO_2 to escape as it is generated. Thus, the total tank volume should be multiplied by .9 (90% of capacity) to determine the actual volume of mash to be prepared.

The second rule to be used in determining the size of the tank or amount of mash to prepare is that approximately 30 to 35 gallons of water are required per bushel of grain meal to be used. Thus, if the tank has a 1,000-gallon capacity, simply multiply the tank volume by .9 to allow for CO_2, and then divide the remaining capacity by 30 to 35 gallons per bushel of grain.

EXAMPLE: Assume a small tank of 1,000-gallon capacity.

Step 1.
1000 gallons
x .9 or 90% Mash 10% CO_2
900 gallons Mash equivalent

Step 2.
900 gallons Mash
÷30 gallons per bushel =
25 bushels of grain meal capacity per batch of mash

These figures are rough estimates and may be adjusted as needed.

The ground grain is conveyed to the cooker and mixed with an initial 15 to 25 gallons of water per bushel to form a slurry.

5. Measuring and Adding Enzymes

When grain or potato feedstocks are used to make ethanol, the starch must be converted to simple sugars by hydrolysis. Although this procedure can be accomplished by either acid or enzymatic hydrolysis, the most common method is the latter.

Enzymatic hydrolysis is usually accomplished in two steps with two different enzymes. The first step is liquefaction, the conversion of starch to water-soluble polymeric sugars, called dextrins, by an enzyme called an alpha-amylase. The second step is called saccharification and is the reduction of dextrins to mono- and dimeric-form by an enzyme called a glucoamylase.

Enzymes are catalysts for biochemical reactions, hence they are not consumed as the reaction proceeds. However, the rate of reaction is dependent upon the number of enzymes present in solution, as well as upon the temperature of the solution. Therefore, to increase the rate at which starch molecules are converted to dextrins, both the amount of enzyme used and the temperature of the solution can be increased. Although there are practical limitations because some enzymes also decompose as a result of heat, the point beyond which decomposition of the enzyme becomes severe is a reasonable upper limit on temperature. With commercial thermally stabilized enzymes, the optimum temperature is generally between 195° F and 205° F. The enzymes produced by malting barley are generally not as active at these high temperatures, and the organisms responsible for producing these enzymes (such as Aspergillus niger) are killed at these high temperatures. Although the enzymes are perfectly functional in the absence of the organism, no new quantities of the enzyme are produced.

Commercial enzymes are marketed both as a dry powder and as a liquid solution. Each manufacturer suggests an optimal use rate to achieve maximum conversion in a minimum time period. These rates of addition are generally specified in relationship to the quantity of carbohydrate to be converted. Since this is known from the previous step, the quantity to be added is computed directly using the manufacturer's directions.

See Tables 4,5,6,7 for additional information

6. Temperature and pH Control During Cooking

Starch can be converted to simple sugars by employing enzymes as catalysts if the proper conditions are maintained. The starch cells must first be ruptured and then broken down into their constituent parts. The rupture of the starch cells occurs when they are placed in water and heated to between 140° F and 160° F. The cells first swell as they absorb water, then eventually burst. Because the starch itself is not soluble in water, the resultant slurry becomes a thick "mush" that is difficult to work with unless a "liquefying" enzyme is present. This enzyme, called alpha-amylase, serves to split the starch molecule into polymeric water-soluble sugars called dextrins. These dextrins cannot be directly fermented, but because they are water-soluble they go into solution instead of further congealing or gelatinizing. Thus, it is important to assure that adequate quantities of alpha-amylase enzyme are present in the mash before heatup begins.

The temperature of the solution can be raised by direct injection of steam, by circulating a hot liquid through internal coils, by condensing steam inside of coils, or by directly placing a fire underneath the vessel. The simplest method from the points of view of control, prevention of charring or burning, and equipment simplicity is direct steam injection. The steam that condenses as the liquid heats merely becomes part of the mash; thus, initial water quantities are held short of final requirements to allow for this accumulation of condensed steam.

Care should be taken to assure that temperatures are raised uniformly to achieve gelatinization. Sudden temperature increases can cause localized gelatinization that can lead to "globs" of gel floating in the mash. Similarly, if temperatures increase very rapidly in any isolated part of the mash, improper and incomplete mixing of the mash may result. This can lead to poor sugar-conversion efficiency. Temperature readings used to control heatup should be taken at a point that is not directly in the proximity of steam injectors or heating coils nor located in a stagnation zone where circulation is incomplete. If possible, multiple temperature readings from different locations in the fermenter should be used to assure that mixing is thorough and temperatures are uniform throughout.

Once gelatinization begins, the heat input rate should be retarded to the point that the temperature holds steady (input just equal to heat loss). Agitation should be maintained and no further temperature increases should be attempted until liquefaction is well underway. This is indicated by a reduction in the viscosity of the solution as the water insoluble starch is converted to water-soluble dextrins. Once liquefaction is well established, the temperature should be raised to the optimum temperature for the liquefying enzyme. Since the enzyme is measured in quantities proportional to that needed to convert a given quantity of starch in half an hour, it is only necessary to hold at the maximum liquefying temperature for this period of time.

A common alternative procedure is to raise the temperature of the mash to boiling in order to sterilize it. Though this may exceed the optimum enzymatic activity range, it usually is not harmful to the enzyme and serves the important purpose of killing most of the competing microbes initially present in the mash.

As liquefaction nears completion, the temperature of the mash is reduced (by adding the rest of the dilution water if an initial high solids concentration is employed) and by circulating cooling water through internal coils or external jackets. Once the temperature falls below 140° F, the cooling water is stopped and the saccharifying enzyme or glucoamylase is added to the solution. The temperature is maintained within the optimal range for this enzyme by periodically adding heat through steam injection or heating coils.

Once saccharification is nearly complete, the temperature of the mash is again reduced by circulating cooling water through internal coils or an external jacket. Once the temperature reaches the proper fermentation temperature, circulation of cooling water is stopped or reduced to the level that just maintains the constant desired temperature. All adjustments are made with respect to the same representative temperature indication. Reference consistency is important for producing results that can be duplicated time after time.

The control of pH during cooking is not as crucial as during fermentation. Nonetheless, each enzyme has an optional pH range at a given temperature, and best results are obtained by balancing pH in the desired range. The pH of the solution will change with time, especially if the mash is boiled (because of the thermal removal of carbonates and bicarbonates). The pH should be continuously monitored with a pH meter unless very small batches are being prepared. In this event, strips of pH paper can be used to determine relative pH. These strips of paper are chemically treated so that when they are dipped into a solution containing acid or base they turn a specific color relative to the amount of acid or base present. This color can then be compared to a reference chart which has a pH value indicated for the shades of colors from pink to blue. Measurements using pH paper are not reliable for large batches and are necessarily a manual measurement hence often overlooked on the frequency usually necessary. In contrast, a pH meter can be installed in a representative location within the mash to provide an indication with high accuracy on a continuous basis. Acid or base additions to maintain a proper balance are easily achieved as the cooking process goes on.

7. Checking for Sugar Conversion

There are both qualitative and quantitative tests which can be performed to determine the adequacy of starch conversion to sugar. Among the simple qualitative tests is a simple visual scan of the mash. Lumps of white material are indications of unconverted starch.

A qualitative test can be performed by using the iodine starch test. The test solution is prepared by dissolving 18 grams of potassium iodide in approximately 700 milliliters of distilled water containing 12.7 grams of iodine. Addition of a small quantity of this solution to a filtered aliquot (sample) of mash will yield a light yellow to light red color if liquefaction is complete. If starch conversion is not complete, a dark blue color will result.

A quantitative test for conversion is made by using a hydrometer that is specific for sugar concentration. The scale on the hydrometer indicates the percentage of sugar in the solution of brew.

8. What to Look for in Gelatinization

The objective of heating starch cells in water is to cause them to burst so the enzymes present in solution can convert them to simple sugars. However, if the "gel" becomes too thick or forms too rapidly, liquefaction can be arrested. If the gel becomes too viscous to stir, the diffusion of enzymes through the material is severely retarded. Among the several remedies available are (1) addition of water to dilute the slurry, (2) reduction of temperature to keep from making the problem worse, and (3) addition of more liquefying enzymes. Each of these methods singularly or in combination may suffice to break up a thick gel. In the event that none of these techniques is successful, a final though undesirable alternative is to continue dilution until the viscosity drops. Then the process can be repeated, but the beer that results is more dilute than normal and the consequences are absorbed throughout the system.

9. Sterilization

Fermentation is the result of preferentially culturing a specific microorganism in the absence of oxygen to produce ethanol. Yeasts are not the only anaerobic microorganisms, however, and as such they must compete with the others present for the available sugar. Yeasts are large cellular organisms that propagate more slowly than smaller bacteria such as Pseudomonas and Lactobaccillus. Thus it is desirable to handicap these other organisms by killing as many as possible by sterilization. Although no sterilization process is 100% effective, methods such as chemical antiseptics and heat treatment are often successfully employed to reduce the populations of competing microorganisms to acceptable levels.

Sterilization by heat treating reduces microorganisms. Stated another way, if holding a mixture at a given temperature for a specific amount of time reduces the microbial population from 100,000 to 10,000, then roughly twice as long is needed to reduce it from 10,000 to 1,000 and so on. Usually, holding a mash at or near boiling for 30 minutes suffices to reduce the microbial populations to tolerable levels.

TABLE V-1

SUMMARY OF FEEDSTOCK CHARACTERISTICS

Type of Feedstock	Processing Needed Prior to Fermentation	Principal Advantage(s)	Principal Disadvantage(s)
Sugar Crops (e.g., sugar beets, sweet sorghum, sugarcane, fodder beet, Jerusalem artichoke)	Milling to extract sugar.	1. Preparation is minimal. 2. High yields of ethanol per acre. 3. Crop coproducts have value as fuel, livestock feed, or soil amendment.	1. Storage may result in loss of sugar. 2. Cultivation practices are not wide-spread, especially with "nonconventional" crops.
Starch Crops: Grains (e.g., corn, wheat, sorghum, barley)	Milling, liquefaction, and saccharification.	1. Storage techniques are well developed 2. Cultivation practices are widespread with grains. 3. Livestock coproduct is relatively high in protein.	1. Preparation involves additional equipment, labor, and energy costs. 2. DDG from aflatoxin-contaminated grain is not suitable as animal feed.
Cellulosic: Crop Residues (e.g., corn stover, wheat straw) Forages (e.g., alfalfa, Sudan grass, forage sorghum	Milling and hydrolysis of the linkages.	1. Use involves no integration with the livestock feed market. 2. Availability is widespread.	1. No commercially cost-effective process exists for hydrolysis of the linkages.

TABLE V-2

BASIC STEPS IN ALCOHOL PRODUCTION

1)	Milling	The starch source (usually corn, wheat, rye, sorghum or barley) is ground into a fine meal (12-16 mesh). This exposes the starch granules and permits suspension and dispersion in the following step.
2)	Slurrying	Water is added to the meal to form a mash (typically 15-25 gallons of water per 56 lb. bushel of grain). The mash is adjusted to pH 6.0-6.5 and the liquefying enzyme, Taka-Therm, is added.
3)	Liquefaction	The mash is heated to gelatinize the starch (170-200° F) and render it susceptible to enzyme breakdown. During this cooking step, Taka-Therm rapidly reduces the viscosity of the mash and the starch is converted into soluble, high molecular-weight carbohydrates called dextrins.
4)	Conversion	The mash is cooled to conversion temperature, (135-140° F). The pH is adjusted to pH 4.0-4.5 and a conversion enzyme, Diazyme L-100, is added. The mash is held long enough to permit some of the dextrins to be converted into fermentable sugars. It is then cooled further to the fermentation temperature (85-90° F). Water can be added to aid cooling to a final volume - about 33 gallons per 56 lb. bushel of grain.
5)	Fermentation	Distiller's yeast is added and the mash is held 48-120 hours. During this time the conversion enzyme continues to break down dextrins to fermentable sugar while the yeast converts these sugars to alcohol and carbon dioxide. The fermentation process produces heat so that cooling is necessary to maintain yeast survival.
6)	Distillation	The fermented mash is heated to vaporize the alcohol, and the vapors are collected and cooled to condense the alcohol back to a liquid. The residue contains the residual grain, spent yeast, and water. The residual grain and spent yeast are generally used in animal feeds. The water is usually recycled.

TABLE V-3

BIOCON'S
SIMPLE "FOUR-STEP" PROCEDURE
For 5 Bushels*

Step I.	Add water to cooker (25 gal/bushel) Add 5 bushels corn (or other cereal) ground as fine as possible. Add 2 oz. CANALPHA (white powder). Mix well. Heat to 200-212° F with constant mixing. Hold for 15 minutes.
Step II.	Cool mash to 150-170° F by adding just sufficient water (5-8 gal/bushel). Add 4 oz. CANALPHA (white powder). Mix will. Hold for 30 minutes with constant mixing.
Step III.	Cool mash to 90° F as fast as possible. Add 2 oz. GASOLASE (fine brown powder). Add 4 oz. BIOCON Special Distiller's Yeast (granulated brown powder). Mix will. Ferment 2-3 days.
Step IV.	Mash now ready for distillation.

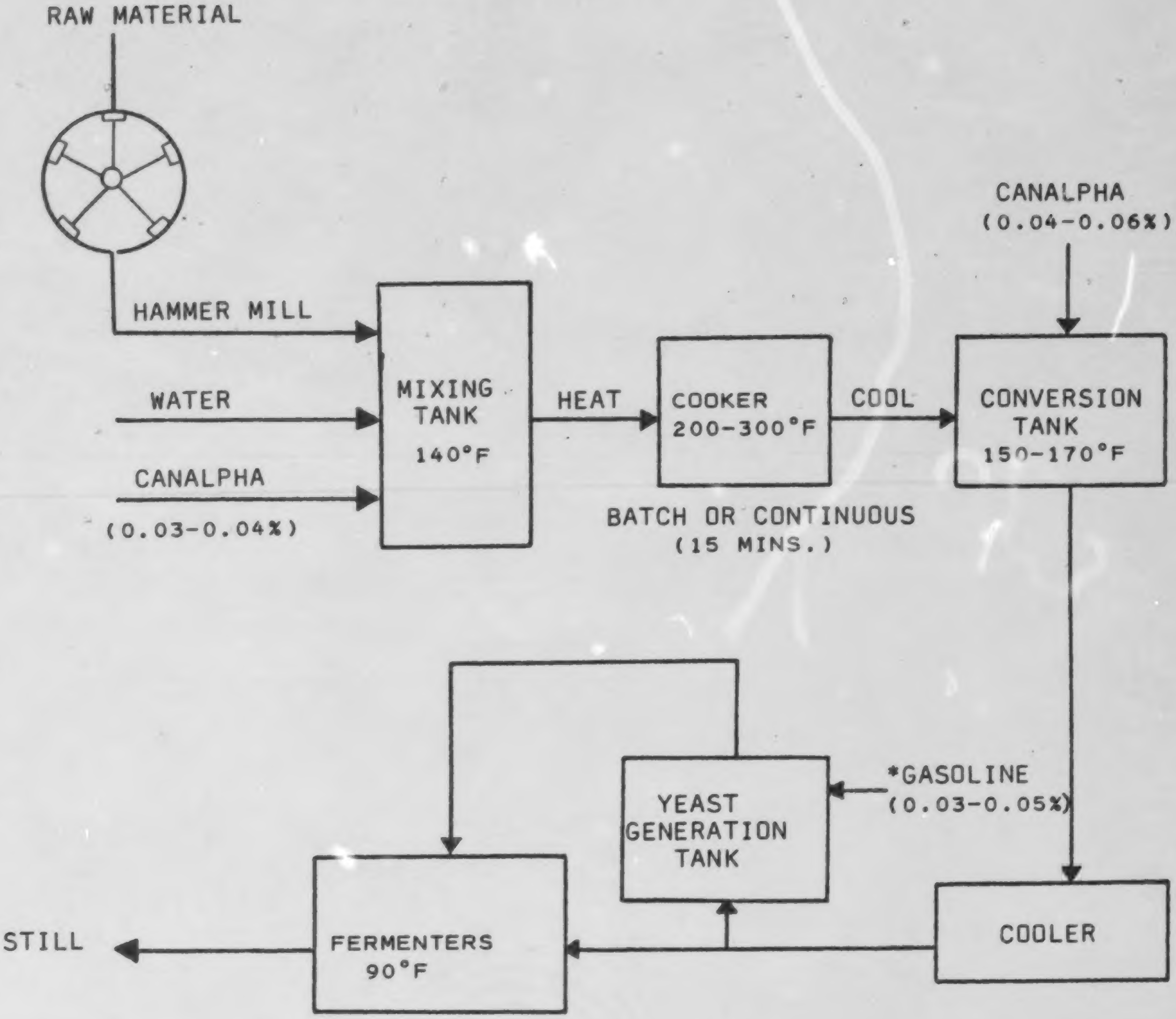
With experience, the above rates may be reduced by as much as 50-60% without loss of yield. With reduced rates and purchasing CANALPHA, GASOLASE and BIOCON Special Distiller's Yeast in quantity, the cost per gallon of 180-proof alcohol will be around 8-10¢. If yeast price is not included, the cost will be 2-3¢ lower.

*For quantities other than 5 bushels, adjust rates accordingly.

Source: Biocon (U. S.) Inc.
261 Midland Avenue
Lexington, Kentucky 40507

TABLE V-4

BIOCON ENZYME CONVERSION PROCESS (CORN, RYE, WHEAT & POTATOES)


RAW MATERIAL
HAMMER MILL
WATER
CANALPHA
(0.03-0.04%)
MIXING TANK 140°F
HEAT
COOKER 200-300°F
BATCH OR CONTINUOUS (15 MINS.)
COOL
CANALPHA (0.04-0.06%)
CONVERSION TANK 150-170°F
*GASOLINE (0.03-0.05%)
YEAST GENERATION TANK
COOLER
FERMENTERS 90°F
STILL

*IN ABSENCE OF YEAST GENERATION TANK, GASOLINE CAN BE ADDED DIRECTLY TO FERMENTER.

Source: Biocon (U. S.) Inc., 261 Midland Ave., Lexington, Kentucky 40507

TABLE V-5

BIOCON Distiller's Active Dry Yeast

Our yeast, a selected strain of Saccharomyces cerevisiae, is especially designed for distiller's use in grain and cellulose derived sugar fermentations. It will give maximum alcohol yields over a wide range of pH's and temperatures.

Recommended usage rate is 2-4 lbs./1000 gallons (5-10 million cells/ml.) of mash when the sugar concentration is between 15-25%.

Optimum mash pH is between 4.0 and 5.5 Optimum temperature is 86° F (30° C) but good yields are obtained between 80° F and 100° F with speed of fermentation increasing with increasing temperature.

Initial fermentation may be accelerated by rehydrating in several gallons of warm (110° F) water per 1 lb. of yeast for 5-10 minutes before adding to the mash.

TABLE V-6

GASOLASE
FUEL ALCOHOL PRODUCTION

Gasolase is a carefully selected blend of enzymes derived mainly from Aspergillus niger and Rhizopus niveus. All of the enzymes incorporated in Gasolase have been approved by the FDA and BIBRA as suitable for ethanol production.

Gasolase is a sophisticated wide-range enzyme system that is more than just a simple spectrum amyloglucosidase from Aspergillus niger. Gasolase incorporates alpha amylase, amyloglucosidase, protease, beta glucanase, cellulase, hemicellulase, pectinase, pantothenic acid, biotin, and a number of other essential vitamins and enzymes combined to give a complete system capable of dealing with the wide range of alcohol production conditions normally encountered in the ethanol production industry. Because of the spread of enzyme activities found in Gasolase, it is available only in powder form, as the stability characteristics of enzymes in liquid form are often limited.

Use Conditions

The optimum point of addition of Gasolase is to the fermentor subsequent to liquifaction of the grain, be it corn, rice, barley, rye, sorghum, potatoes, or other starch sources. The rate of addition of Gasolase depends on the cereal grind (as fine as possible); the type of cooking-whether it is continuous or batch; the efficiency of the cooking, etc. Tentative use rates are outlined. With increasing efficiency, these may be reduced.

Batch Cook

Preliquify the grain by using 0.05% of the "as is" weight of the cereal (potatoes, 0.02%-0.03%) of Canalpha bacterial alpha amylase. Cook, cool down, and postliquify at 160-175° F with 0.1% Canalpha for 15-30 minutes. Cool to fermenting temperature, (85° F ± 5° F). Add 0.05% Gasolase in the form of a cold water slurry. Add Biocon Distiller's Active Dried Yeast at the same time.

Note: Gasolase is effective up to 120° F but Yeast may be inactivated at temperatures over 100° F.

Continuous Cook

For continuous cooking, which is much more efficient than batch cooking in terms of availability of starch for conversion, lesser rates of Canalpha may be used and an addition rate of 0.04% Gasolase is sufficient.

TABLE V-7

CANALPHA
Fuel Alcohol Production

Canalpha is a B. Subtilis Alpha Amylase from a specifically selected strain of the organism, which will liquify economically and effectively at pH 4.8-7.5.

Canalpha ensures liquifaction of starches and production of dextrins, which are intermediate products between starch and sugar. Liquifaction performance graphs attached clearly show Canalpha performance characteristics.

Canalpha has an activity of 180,000 alpha maylase units per gram and a controlled viscosity to ensure even metering operations.

Use Recommendations

In order to ensure mobility and ease of mixing and transferring of the mash, at all times, Canalpha is used as a preliquifier in fuel production operations when using corn, wheat, milo, rice, potato, or other starchy materials. Canalpha should be used at a rate of 0.05% of the "as is" weight of grain, holding at temperatures between 160-175° F for elimination of thickening prior to cooking.

For the same reasons, it is recommended that post liquifaction of a cooked fuel alcohol mash be made by using 0.1% by weight of Canalpha, based on the "as is" weight of grain, holding at temperatures of 160-175°F, for up to 30 minutes before cooling down to fermenting temperature (36° F ± 5° F). This addition of Canalpha after cooking ensures that the mash is fluid right to the fermenters.

C. Fermentation

The key to successful ethanol production is good fermentation techniques. Ethanol lost or not produced in this step can never appear in the product tank, The keys to ethanol production all lie in maintaining the proper yeast environment. Although the two most basic factors are maintenance of pH and temperature, there are many subtle considerations which affect the fermentation.

1. Establishing Initial Fermentation Conditions

Early in the fermentation process there are several desired occurences:

a. Rapid yeast propagation.

b. Minimal sugar loss to competing microbes.

c. Rapid yeast acclimatization.

d. Rapid shift from facultative to anaerobic metabolism.

The first condition is achieved by reducing the temperature to less than 95°F and providing the nutrients required for yeast propagation. Among these are appropriate quantities of calcium, magnesium, and potassium, as well as assimilable forms of nitrogen and phosphorous. Most grains contain sufficient quantities of each of these, but mashes made from extracts of sugar crops may be deficient in any or all of these areas. Supplemental nutrients can be provided with sterilized urea or by direct addition of proteins (for their amino acids) and grain germ. Conditions can be further assured by carefully removing or neutralizing chemical contaminants such as sulphites (which severely impede yeast propagation and metabolism). Yeast propagation is greatly enhanced when conducted in the presence of oxygen because 19 times more energy is released in the metabolic process in the "Krebbs" cycle than in the Embden Meyerhoff pathway. Thus, it is important that the amount of oxygen dissolved in the solution is great. As the oxygen is consumed the process automatically becomes anaerobic and ethanol production begins. If bacterial contamination is considered eminent, then appropriate antibiotic treatment of the fermentation solution is recommended. (Penicillin is added at the rate of 1 gram per 300 gallons of solution.)

A significant factor in rapid yeast propagation is the presence of an initially large population of viable yeast cells at the start of the fermentation. The results of experience indicate that an initial inoculum of 3% to 5% of the fermenter volume is sufficient to achieve rapid fermentation of the substrate, or innoculate with the manufacturer's recommended rate. This may be of necessity with small scale units.

Sugar loss to competing microbes can be minimized by adjusting the pH to less than 5.0. In this range, the most prevalent competing bacteria, Lactobacillus and Acetobacter, are non-functional.

Rapid yeast acclimatization can be achieved by yeast recycle from batch to batch, by cascading yeast forward a portion of the yeast from each batch to the next subsequent batch.

2. Measurement and Control of pH

The steps that the operator should follow after the mash is transferred to the fermenter start with adjustment of pH. Ethanol production is most strongly favored under acidic conditions, but significant fluctuations in pH after fermentation begins suppress yeast activity.

The pH of the solution can be determined by using pH paper, but its limitations should be recognized. The samples are not necessarily representative because the measurement can only be taken from the top of the mash. Furthermore, the accuracy of each measurement is dependent upon the operator's ability to match hues and colors of the pH paper to the calibrated reference. Errors as great as ±10% are common when using pH paper.

The pH of the solution can also be determined by an automatic pH meter. This device uses a specifically designed electrode to measure the pH of the solution at its point of location in the solution. The accuracy attainable with a pH meter is fairly high and indications of pH are continuously available.

Although pH adjustments can be calculated by using the concentration of the acid or base, the initial pH of the solution, and the total amount of solution, actual results can vary depending principally upon the presence of carbonates and bicarbonates. Thus, the surest way to achieve the desired pH is to make minor adjustments, followed by stirring and then observing the pH that results. After this procedure has been followed, the quantity of acid or base that is required to effect a given pH change will be known from the previous experience. Care should always be exercised when making adjustments because the carbonate concentration in water can vary seasonably, causing the amount of acid required to neutralize it to change in direct proportion.

Also, certain yeast manufacturers make specific recommendations to pH range and necessary adjustments. Always follow directions.

3. Control of Temperature

Yeasts tolerate a fairly wide range of temperatures; however, once they have become acclimated to functioning at a specific temperature, the best results are obtained by keeping variations in temperature to less than 2°C on either side of the setpoint. Since the anaerobic metabolism of the yeast releases energy as it proceeds, the mash must be actively cooled, especially during the summer months, to keep the temperature from rising too much. If the cooling is done by circulating water through internal coils, the flow rate should be monitored and adjusted continuously since the rate of heat generated changes directly with the rate of fermentation. Initially, the rate of fermentation is quite slow but the amount of heat given off as the yeast aerobically propagates is quite large. As the oxygen is consumed and the yeast propagation subsides, the rate of heat generation is also reduced. After a period to allow anaerobic fermentation to become well established, the rate of heat generation again increases as the rate of fermentation increases as shown in Figure V-1. Once the maximum fermentation rate is achieved, the rate gradually tapers off and decreases more and more rapidly as the concentration of alcohol increases.

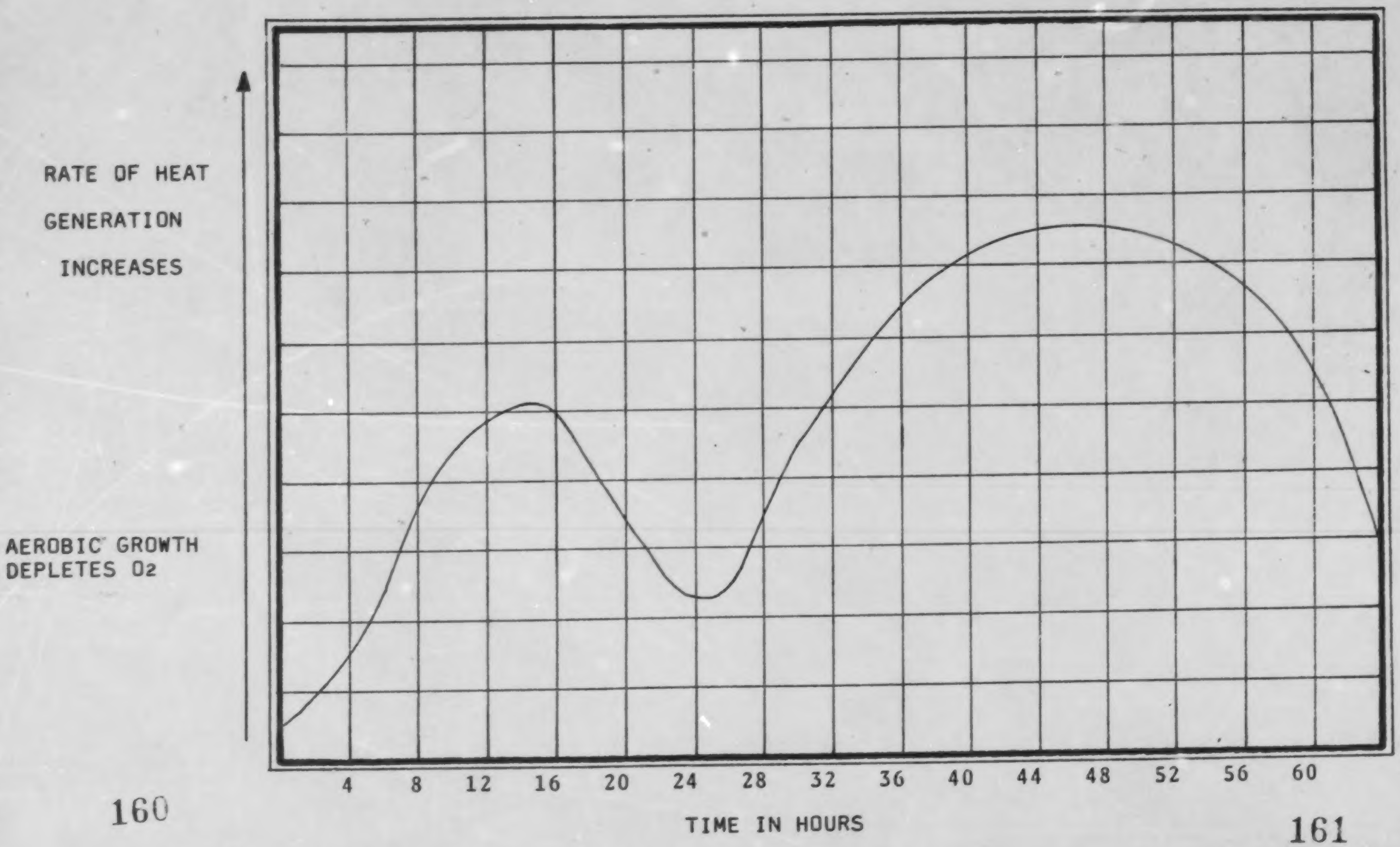
Because the rate of heat generation varies continuously throughout the fermentation, manual cooling adjustments are generally impractical. Automatic controls are relatively simple and quite reliable. The basic components of such a system are (1) a temperature sensor such as a thermocouple, (2) a controller which processes the signal from the sensor and activates the regulating devices, and (3) a regulating device such as a valve that can deliver flow at a variable rate. When the temperature sensor indicates the temperature is rising above prescribed limits, the controller sends a signal to the valve, causing it to open wider to increase the flow of cooling water.

4. Determining the Size of Yeast Inoculum

To an extent, the rate at which a given quantity of sugar can be fermented to produce ethanol is dependent upon the amount of yeast initially present. This is analogous to several workers being able to accomplish a given task in less time than one. But in the same sense that there is a fallacy in presuming that if one man can build a brick wall in an hour, that 60 men could build it in a minute, there is a point of diminishing returns. The expense for extremely large yeast inocula can adversely impact production economics. On the other side of the coin, the long fermentation times that result from a yeast inoculum that is too small can also adversely affect production economics by reducing effective production capacity.

FIGURE V-1

ANEROBIC FERMENTATION - ALCOHOL CONCENTRATION INCREASES



The appropriate amount of yeast to pitch in is dependent upon the yeast conservation techniques that are employed. Yeast recycle and yeast cascading reduce the total rate of yeast pitched by the amount returned from previous batches. In general practice, the inoculum of viable yeast cells to each batch should be 15 to 20 million cells per milliliter using between 3% to 5% of the fermenter volume as the size inoculum. Follow manufacturer's recommended innoculation rates.

5. Analyzing Fermentation Progress

There are a variety of factors which can suppress a fermentation. The osmotic pressure of the mash can be too high, the pH can be too high, the temperature can be too high or too low, there can be too much oxygen present, there can be insufficient nutrients available for yeast propagation, there can be other microbes present that propagate more rapidly than the yeast, and there can be a variety of organic and inorganic chemicals that stifle yeast metabolism. The results of any of these range from no fermentation activity at all to production of a whole variety of products other than ethanol.

The presence of lactic acid and acetic acid-forming bacteria is indicated by a rapid decrease in pH. The mash will change from a mildly sweet tasting liquid to a very acrid or sour taste. (The pH of a mash will naturally reduce gradually as the fermentation proceeds because of the formation of carbonic acid by the CO_2 generated. However, this change in pH is much more gradual than that observed with acid forming bacteria.)

The presence of sulphite in solution will more likely cause formation of glycerol rather than ethanol. Glycerol formation is also favored at high pH although the more common principal fermentation product is acetaldehyde, the ethanol precursor in the Embden-Meyerhoff pathway.

Copper ions in solution can have significant adverse effects on yeast metabolism. Concentrations above 0.4 milligrams per liter can retard fermentation and at 15 milligrams per liter the fermentation ceases. Such high concentrations of copper ions may be encountered if uncoated copper tubes or uncoated copper vessels are used in fermenters.

Aluminum concentrations above 25 milligrams per liter will likewise suppress fermentations. Such concentrations in an aluminum fermenter would not be expected unless the fermentation is conducted in the presence of relatively large amounts of lactic or acetic acid.

Volatile organic compounds are continuously released by some types of plastic and fiberglass. Just as glue sniffing is lethal to humans, these plastic solvents can be detrimental to the yeast.

A successful fermentation is indicated by vigorous rate of carbon dioxide generation. The change in specific gravity of the beer is gradual and actually quite small; hence, Brix hydrometer readings are of marginal value in measuring fermentation progress. The end-point of fermentation is indicated when the sugar in the mash is depleted. Although there are chemical tests for determining sugar concentration, a simple qualitative test is to merely taste a very small quantity of the mash. A sweet taste indicates unconverted sugar and the fermentation should be continued if CO_2 is still being generated. Caution is advised if this method is used, especially if each batch is not sterilized. A mash is an ideal culture media for all kinds of bacteria, some of which are disease-producing.

Sugar test tape (diabetic tape) may also be used as an indicator for conversion. Early test results using test tape will differ significantly from final tests.

6. Providing Yeast Nutrients

In malt and grain mashes there is sufficient assimilable nitrogen, phosphate, and magnesium for yeast to propagate at maximal rates. When some yeast recycling is employed and thin stillage is used as makeup water for the preparation of mash, additional buffering capacity, nitrogen, and phosphate are provided.

When mashes are prepared from substances low in initial protein, the amount of nitrogen that can be assimilated is severely limited. The required nitrogen can be provided in the form of ammonium salts and sterilized urea. With most tuber and sugar mashes it is rarely necessary to add phosphate, potassium, or magnesium. The addition of nitrogen and phosphate should be done with care as indicated by extended yeast propagation phases. Excess phosphate and nitrogen, particularly in the form of ammonia, can be quite detrimental to yeast.

7. Recognition of Fermentation Problems

The generation of carbon dioxide is the strongest indication that a biological metabolism is underway. If there is no way for oxygen to become entrained in the mash, the process is proceeding anaerobically. If the predominant microbe is the yeast being cultivated and the conditions are properly adjusted, the odds favor the production of ethanol. Because the processes involved are extremely complex, there can be no absolute guarantees.

The indications of a fermentation breakdown are multiple; some subtle, some obvious. An extremely foul odor from a fermenter vent indicates that the wrong microbe is predominating. If this occurs early in a fermentation, recovery can be effected by resterilizing the batch. Although the yeast is killed and therefore lost, the sugar can still be converted to ethanol. A successful fermentation will smell "yeasty" like a bakery or brewery.

A bad fermentation can be indicated by changes in the color of a batch. Cloudy (milky) or brackish mashes (especially grain mashes) may be fostering undesired microbes. DO NOT PERFORM SUGAR TASTE TESTS ON ANY SUSPICIOUS-LOOKING OR SUSPICIOUS-SMELLING MASHES! AMONG THE COMMON MICROBIAL CONTAMINANTS, ESPECIALLY WITH TUBERS AND ROOTS, ARE CLOSTRIDIUM BOTULINUS, THE MICROBE THAT IS RESPONSIBLE FOR BOTULISM POISONING, AND CLOSTRIDIUM TETANUS, THE MICROBE THAT CAUSES "LOCKJAW"!

Slower fermentation activity can be expected if the temperature of the batch is allowed to drop below 27° C and stay there. Similarly, if the pH is allowed to remain high, acetaldehyde or glycerol will be produced in larger quantities than ethanol.

Large quantities of inert material, dirt, ash, etc., not only increase the osmotic pressure of solution but also can shift the biological reaction balance in favor of glycerol production.

A fermentation with a pH lower than 3.5 can be expected to proceed quite slowly. To increase the yeast metabolic rate and also to protect process equipment from corrosion, the pH should be adjusted back to above 3.5.

D. Distillation

Once a beer has been produced, the distillation system can be started up. The procedures for starting and operating batch and continuous distillation systems vary markedly and thus are discussed separately.

1. Batch Distillation

Batch distillation equipment are basically rectification columns. A "pot" of mixture is boiled and condensed under reflux conditions until the amount of ethanol remaining in the pot is acceptably low and the concentration of the ethanol in the product receiver is acceptably high. The number of theoretical stages and the reflux ratio used serve to define the level of separation which can be achieved in a single pass with such an apparatus. Each time the process is repeated effectively adds to the number of theoretical stages employed.

In a batch still the concentration at any point inside the column is continuously changing. If the pot is allowed to boil for an even second, the amount of ethanol in the pot has been reduced by the amount that was evaporated, thus the concentration changed. As the concentration of ethanol in the pot is reduced, the boiling temperature of the mixture is increased. At atmospheric pressure, a batch distillation will begin (for a 10% (v/v) beer) at 197° F and will reach the azeotrope at 209° F.

a. Setting and Controlling Boil-Up Rates

The rate of boil-up is controlled by the amount of heat input to the system. High boil-up rates result in high vapor velocities in the column. A properly designed column will maintain vapor velocities at no greater than the height equivalent of a theoretical stage per second (distance in feet).

Boil up rates should be relatively slow when approaching 200° F and held constant and unfluxuating throughout the initial phase of the boil-up. Properly placed thermometers on the column will indicate the rise in equilibrium as the vapor ascends through the packing material or the plates. Once the boiling point of ethanol (173°F) is reached at the top of the column, a high proof vapor should be ready to move into the condenser for reliquification.

b. Setting and Controlling the Reflux

Reflux is the reliquification of ethanol vapor before it enters the condenser, thus causing the liquid to descend the stripping column. This liquid, which is relatively high in ethanol percentage, enriches the vapors that are ascending the column from the batch tank. This enriched vapor is then allowed to pass into the condenser at a slow rate for reliquification. The amount of vapor being refluxed as compared to the amount being allowed to pass into the condenser, establish a reflux ratio. For example, a 9-1 reflux ratio would mean that 9 times as much liquid is descending the column as is being passed to the condenser as a final product. Reflux ratios generally range from 4-1 to 9-1 for optimal results.

Refluxing is accomplished by the use of a partial condenser of some type ahead of the final condenser. A properly designed still should have a reflux condenser capable of completely stopping the flow of liquid to the final condenser. The temperature of the vapors entering the final condenser should adhere as closely to 173° F as possible for the best results. Only with proper refluxing can 192% proof ethanol be obtained from a distillation unit.

Once the vapor has been recondensed in the final condenser, it should exit into a storage vessel. The last temperature gauge should be located in the product line ahead of the storage vessel. This gauge should read as near to 60° F as possible and should never read above 110° F. The alcohol temperature can be decreased by increasing the flow rate of cooling liquid through the final condenser. (See Figure V-2)

2. Continuous Distillation

Once a continuous distillation system reaches steady-state conditions, the concentration and temperatures at any given point in the system remain constant. Thus, the feed rate is constant, the boil-up rate is constant, the vapor velocities remain constant, the reflux flow is constant, the condensation rate is constant, and the product flow remains constant. Each of these conditions can change as a result of external influences and a new set of equilibrium conditions will result. A decrease in the ethanol concentration of the beer will result in a required increase in the boil-up rate and increased condensation rates. A change in the temperature of the cooling water will change the rate of condensation.

The steps for starting up a two-column distillation system as shown in Figure V-3 are:

Step 1. Starting Condenser Cooling Water Flow at Design Rate

None of the system is yet operating so no condensation is taking place. However, as the system comes up to temperature, it is necessary to prevent ethanol vapor flow directly out the noncondensible gas vent in the condensate receiver.

Step 2. Steam Purge

The operating temperature of a continuous distillation system is near the boiling temperature of water. Since proper operation of the system requires constant temperatures, the entire system must be warmed from room temperature to operating temperature before any beer is introduced.

A second important reason for a steam purge is the removal of oxygen and inert gas from the system. The oxygen poses a system fire hazard and the nitrogen present in air will cause excessively high initial vapor flow rates if it is not removed.

The steam purge is accomplished by opening the vent on the top of the rectifying column and starting steam flow into

FIGURE V-2

CONDENSER SYSTEMS

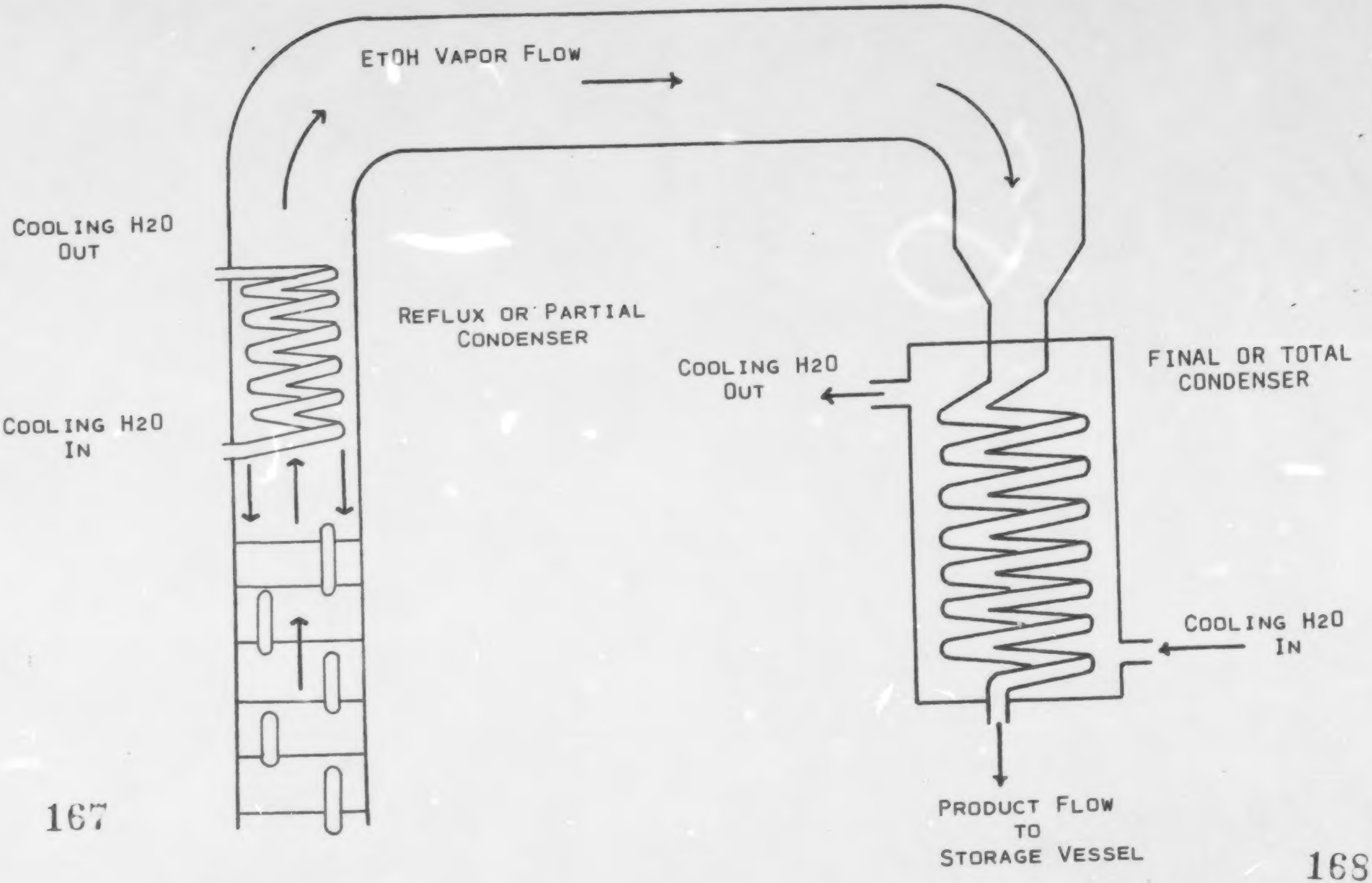
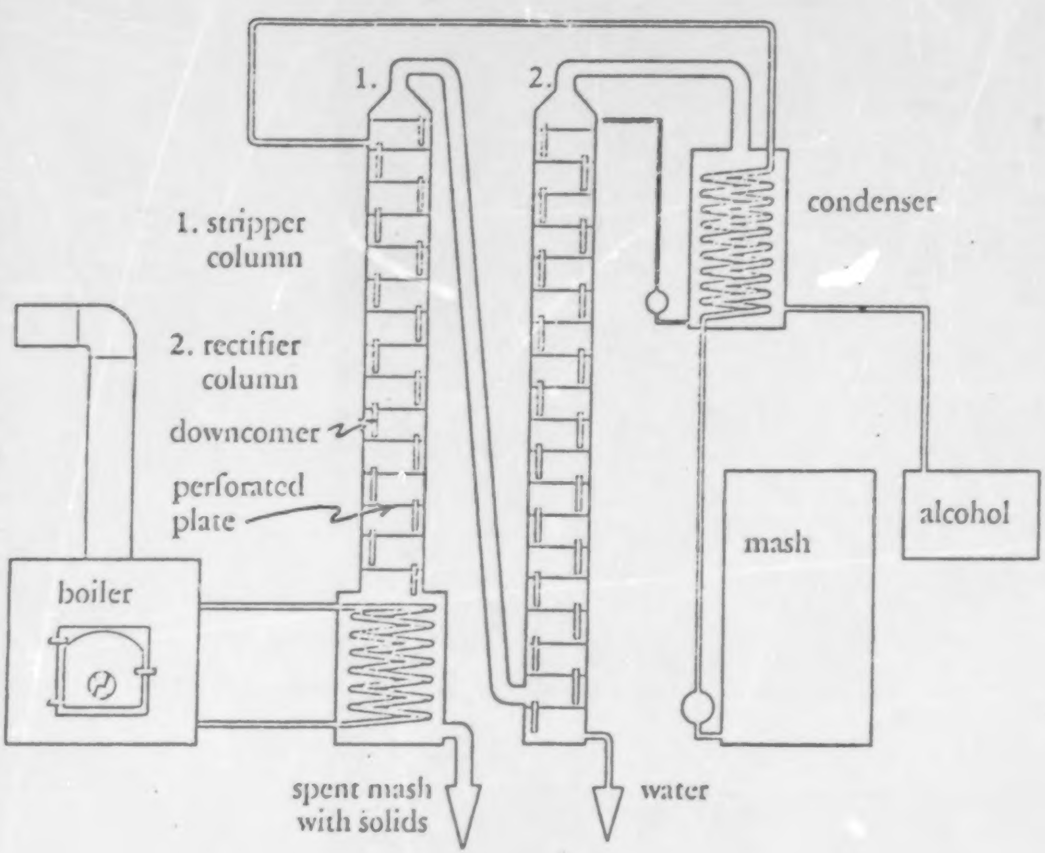
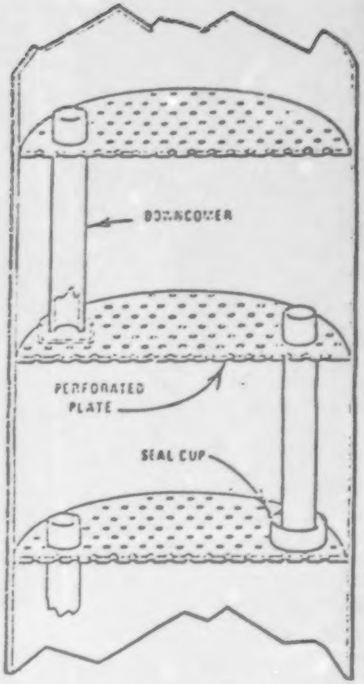

ETOH VAPOR FLOW
COOLING H2O OUT
REFLUX OR PARTIAL CONDENSER
COOLING H2O IN
COOLING H2O OUT
FINAL OR TOTAL CONDENSER
COOLING H2O IN
PRODUCT FLOW TO STORAGE VESSEL

FIGURE V-3

Diagram of 2-Column/Continuous Feed Still


1.
2.
1. stripper column
2. rectifier column
downcomer
perforated plate
condenser
boiler
mash
alcohol
spent mash with solids
water


DOWNCOMER
PERFORATED PLATE
SEAL CUP

PERFORATED PLATE COLUMN

the bottom of the stripping column. The purge should be contained until the entire column reaches operating temperature, then the vent valve should be closed.

Step 3. Pump Beer into Stripping Column

Once the column is near operating temperature, beer is pumped into the stripping column. As the beer enters, part of it will immediately flash to vapor and part will overflow to the tray below the feed tray, and so on down the column. If continuous flow does not produce a liquid level in the site glass at the bottom of the column within a minute or two after beer feed is started, the steam rate should be reduced. If the liquid level rises rapidly to the top of the site glass, the steam should be increased until the level stabilizes in the center of the site glass.

The stillage pump should be started once the liquid level in the bottom of the stripping column is established. This will serve to preheat the beer entering the column. The reflux lines between the columns and between the condensate receiver and the rectifying column should be open but the reflux pumps should remain off.

Step 4. Establish Reflux

Once a condensate level is achieved in the condensate receiver, the primary reflux pump can be started, but the flow should be throttled. When reflux is established the vapor flow rate to the condenser is reduced. The throttle valve in the reflux line should be adjusted to maintain a liquid level in the condensate receiver and a liquid level in the site glass at the bottom of the rectifying column. Once a liquid level is established at the bottom of the rectifying column, the secondary reflux pump is started. This will further reduce vapor flow rates and the steam rate will probably have to be increased to maintain consistent liquid level in the bottom of the stripping column.

Until the system reaches equilibrium, the steam flow (boil-up rate) and reflux throttle valves must be adjusted periodically. If the system is properly designed, the steam flow rate reflux flow will level off very nearly at the design specifications.

3. Checking and Adjusting Product Quality

Among the simplest and least expensive ways to determine the ethanol content of the mix product is the use of a "spirit hydrometer". A spirit hydrometer is a stemmed glass bulb with ballast to give a specific buoyancy. It floats vertically in a liquid and the depth at which it rides depends upon the density of the solution in which it is placed. The less dense the solution the deeper it rides. The hydrometer has a calibrated scale clearly visible and permanently attached. The point on the scale that coincides with the liquid surface is the hydrometer reading. If the reading is taken at 60° F, the reading will indicate the ethanol proof of the mixture. If the reading is made at any other temperature, the proof must be computed from standardized tables such as those presented in Appendix A.

If a test of product indicates a proof lower than desired, the product can be recycled to the rectification column. The reflux ratio should be increased to increase product quality.

4. Checking for Ethanol Losses in the Stillage

Measurements of the specific gravity of the stillage are not as reliable an indication of alcohol content as results with the same measurement of ethanol product. The inaccuracies primarily stem from the presence of dissolved and entrained solids in the stillage, as well as the presence of soluble acids and proteins. Ethanol losses can be approximated using a hydrometer, but the indications should be interpreted in light of these factors.

5. Problems

Neither a batch still nor a continuous still operates without occasional problems. This section indicates some of the things that can be expected and possible remedies in their event.

a. Protein Buildup

Beer made from grain contains a significant amount of soluble and entrained protein as well as a variety of fibers and generally nonfermentable materials. As the beer is distilled, these materials (principally the protein buildup on the stripping column internal) surface. The longer the distillation run the greater the buildup gets, until eventually the holes in trays become plugged and the vapor paths in packed columns become blocked. When this occurs the column is rendered useless but the effects on distillation efficiency are felt before complete blocking occurs. As the holes in a sieve tray become more and more constricted, the overall cross sectional area for vapor flow is decreased. This in turn increases the vapor velocities through the plate. Eventually a point is reached where vapor condensation no longer occurs on the plate and the efficiency of each plate correspondingly drops. The overall effect is the same as removing several theoretical stages from the still.

The protein buildup is a rubbery coating that develops on all internal surfaces in the stripping section of a continuous system or in the first several stages of a batch system. The rate of buildup is, of course, dependent upon the still throughput rate. A still producing 25 gallons of 190 proof ethanol per hour from grain beer can anticipate a significant protein buildup within five to seven days of continuous operation.

The protein buildup can be removed by acid washdown, although this poses corrosion problems for the still. A preferred method is removal of stripping column internals and directly scrubbing them down with wire brushes and steam. Time lost in production can be minimized by having a spare rack of trays which can be inserted in the still. Thus, while one set is being cleaned the other is in service.

b. Changes in Ethanol Concentration in Beer

Ideally, every batch of beer brewed is exactly like its predecessor. Thus, adjustments are never required in still operations. In reality, no two batches of beer are exactly alike. To the extent possible, a homogenization occurs in the beer well which blends some of the beer from one batch with that of a successive batch.

When the inevitable batch of beer with a low ethanol concentration occurs, the still conditions must be adjusted to handle it. The boil-up rate must be increased slightly and the reflux ratio should be increased. Adjustments should be made and product quality checked to assure that they are sufficient. If the product proof begins to drop further, increases in both the steam rate (boil-up rate) and reflux ratio are indicated.

c. Column Flooding

Flooding occurs when the rate of liquid overflow on a tray is greater than the downcomer to the plate below can carry. As the liquid level on the plate rises, the flow through the downcomer increases as a result of the increased hydrostatic pressure. This increased overflow rate initiates a flooding problem on the plate below and so on down the column.

A common cause of column flooding is a drop in feed composition without an according increase in the steam rate. The higher concentration of water, which requires more heat to vaporize than water, results in an imbalance between the vapor flow and the liquid overflow.

Column flooding can be controlled by reducing the feed rate if the flooding is occurring in the stripping section, by reducing the reflux ratio if occurring in the rectifying section, or by increasing the steam rate. Care should be taken to assure that reductions in reflux ratio do not adversely affect product quality.

d. Column Plugging or Channeling

Both plugging and channeling cause an uneven distribution of vapor flow in the column. This in turn reduces the efficiency of each plate.

Common causes of plugging in a paced column are (1) lodging and precipitation of solid material among the packing, (2) breakage, (3) compaction of packing material, and (4) scum formation as a result of protein buildup. Although the cause of blockage can be sometimes removed by backflushing with water, steam, or sometimes acid solutions, persistent plugging problems require removal of the packing and direct cleaning.

The most common cause of column plugging in a sieve tray column is protein buildup. This is closely followed by hole blockage by nonfermentable solids in the beer. Fibrous material such as potato skins or grain hulls can form a mat over the holes in the tray. A washdown with a strong caustic solution is often effective for cleanup, but in the long run, a direct scrubbing of column internals is often required.

In continuous distillation columns, a problem called "fusel oil blocking" can develop in the rectification section. This effect is the result of buildup of fusel oils inside the column. Fusel oils are generally higher alcohols, some of which are less volatile than ethanol but more volatile than water. Thus, they vaporize as they are fed into the column, but the reflux causes them to condense before they can exit the column. The point of condensation usually occurs within a three or four-plate range in the column. Determination of exactly which plates this occurs on depends upon the number of theoretical plates and the reflux ratio.

Fusel oil blocking is indicated by a significant and persistent increase in the pressure differential from the bottom of the rectification column to the top. Fusel oil blocking can be relieved by installing drain ports or taps on the plates where blocking is most likely to occur. When a change in pressure differential indicates fusel oil blocking, the drain ports can be opened and the liquid level can again be reduced to the normal operating range.

Fusel oil blocking only occurs to any significant extent in high volume stills capable of producing 185 to 190 proof ethanol which are continuously operated for sustained periods.

e. Changes in Product Quality

A sudden drop in the proof of the ethanol product can be caused by several factors: a drop in the steam rate, a drop in ethanol concentration in the feed, a drop in the beer inlet temperature, a reduction in reflux ratio, or a reduction in plate efficiency.

A drop in the steam rate can be caused by an unnoticed change in the caloric value of the fuel, by a reduction of the heat transfer coefficient in the boiler (or the reboiler if one is employed), by malfunction of a controller or valve, or by a blockage in the steam line. Many commercially available boilers have instrumentation and control systems that compensate for changes in fuel caloric value or reductions in heat transfer coefficient so that a constant supply of steam can be delivered. Reboilers, however, are not commonly available with feedback controllers to control boil-up rate. Further, because reboilers necessarily contain a liquid that is high in suspended and dissolved organic matter, the potential for fouling and tube plugging is great. Both of these factors cause reductions in heat transfer coefficients which in turn reduce boil-up rates.

A drop in ethanol concentration in the beer feed is the result of a poor fermentation of dilution. In most cases poor fermentations are known and the required system adjustments can be anticipated. Unwanted dilution can be caused by direct water leaks into the beer well or by leaks in the beer/stillage heat exchanger. If a leak is suspected in the beer/stillage heat exchanger, the exchanger should be removed from service and drained. Leaks of any consequence can be determined by statically applying water pressure to the tube side (connect one end to water supply and block the other end). If a leak exists, water will begin to flow out of the shell side ports.

A drop in feed inlet temperature can be caused by low heat transfer coefficients in the beer/stillage heat exchanger, by lower than normal stillage temperature or flow rate, by colder than normal beer well temperature, or by plugging in the beer/stillage heat exchanger.

Reductions in reflux ratio are most commonly caused by inadvertent changes in manual throttle valve settings in reflux lines (by pipe vibration or by accidental bumping) or by changes in reflux pump discharge capacity. The latter can be caused by impeller wear or damage, leaks in pump seals, or blockages in the suction or discharge lines. Pump seals should be checked for leakage as part of routine maintenance procedures.

Reductions in plate efficiency are generally the result of vapor bypass or uneven vapor-liquid distribution. In sieve tray columns, any deviations from vertical alignment will cause an unequal liquid distribution on the plate. The vapor will preferentially pass through the shallower liquid depth without contacting the majority of the liquid.

Improperly fitting trays that leave gaps between the column walls and the trays provide a conduit for vapor bypass and uncontrolled liquid overflow. Both reduce plate efficiency.

Packed columns are particularly susceptible to channeling or to the establishment of separate vapor and liquid flow paths. These tendencies can be overcome by installation of distribution plates and skirts which divert liquid flow away from the walls where it tends to build up and vapor flow away from the center which it prefers.

f. Troubleshooting

If something goes wrong, a systemmatic method of troubleshooting is important to save production losses and maintenance expenses. The cause of a breakdown is not always obvious and the obvious suspect is not necessarily the cause. Each system has a hierarchy of interactions with other systems and a hierarchy of functions that occur within the system. The information required to establish the cause of a malfunction is: (1) the number and type of interactions of other systems and (2) the physical phenomena which occur within the system. With this information, a diagram of causes and effects for each system can be prepared. Then in reviewing these in light of known external influences, the key question to be answered is: "What changed to cause this event?"

EXAMPLE: A continuous distillation system is operating at a steady state rate of 25 gallons of 190 proof ethanol production per hour. At 1:30 p.m. a drop in product proof is noted. A check of the fermentation log shows that the batch completed at 6:00 a.m. was about 1/2% lower ethanol concentration than the previous batch. The reflux in this system is controlled by a partial condenser and the cooling water is circulated to a cooling tower. The outside air temperature has risen from a reading of 72°F at 6:00 a.m. to a current reading of 97°F. All system flow rates are unchanged in the last 12 hours. What is the most probable cause of the observed product quality change?

The first step is to assemble a list of the physical factors which influence ethanol product quality. The information available indicates that nothing has changed that would affect plate efficiency or steam rate. A minor change has occurred in the feed ethanol concentration but the effect would not be expected to be significant. The most probable cause in an effective reduction in reflux flow due to the fact that the efficiency of the partial condenser is impaired by a higher temperature of the cooling water. The remedy is thus to increase cooling water flow during the hot part of the day.

6. Vacuum Distillation

The use of vacuum applied to distillation is currently being actively investigated by many research groups. The use of vacuum causes significant savings in input Btu. However, several problems are encountered that make vacuum distillation difficult. The first is caused by the presence of noncondensible gases pulled along in the mixture. The presence of fusel oils causes the second problem.

The noncondensible gas cause a problem in a vacuum distillable column because the volume increases as the pressure drops. Because the volume of the vapor also expands with a decrease in pressure, the diameter of the still should be increased to maintain the desired gas velocity in the column.

The azeotropic mixtures formed by the fusel oils present about the same problem in vacuum distillation as they do in normal distillation. If they are withdrawn from the plate on which they accumulate they flood the column.

Vacuum distillation units may be built and may also be purchased from several manufacturers, but thorough investigation of this type of distillation should be done before one gets too involved. It has also become apparent that vacuum distillation works better with packed column batch typed distillation units than continuous units.

E. Ethanol Drying

Normal distillation procedures can be used to produce a mixture that is 95% ethanol and 5% water by weight. Beyond this ratio, distillation can be continued indefinitely with no change in composition. Since "dry" or anhydrous ethanol is required to assure a stable blend with gasoline, it is necessary to remove most of this remaining water. There are three proven means for doing this: (1) azeotropic or ternary distillation, (2) use of selective chemical dessicants, and (3) use of molecular sieves. The most common method is the first.

1. Azeotropic Distillation

The reason ethanol and water cannot be further separated once an azeotrope is reached is because at azeotropic conditions the relative volatilities of ethanol and water are the same. These relative volatilities can be changed by either changing the system pressure or by adding another component or other components to the mixture. System pressure can be accomplished by drawing a vacuum on the system. Adding a compound such as n-hexane to the mixture will also change the relative volatilities of ethanol and water under azeotropic conditions. Neither method is without its problems.

Certain compounds can be added to the 190-proof mixture to cause a desired change in the relative volatilities of ethanol and water. Benzene and n-hexane are two compounds that have this desired effect and can be put to practical use to distill water from ethanol.

The first commercial application of azeotropic distillation was the dehydration of ethanol with benzene. This use is still one of the major applications of azeotropic distillation today.

An advantage of benzene in azeotropic distillation is it virtually cannot mix in water: ethanol is more soluble in benzene than in water. Therefore, the benzene and ethanol can be decanted from the water without an extra distillation step.

A two-column system can be used for separation of the ethanol and water. The presence of benzene serves to increase the relative volatility of the water. Thus when the feed enters the first column, most of the benzene and water vaporizes along with some of the ethanol. There are a few plates of rectification above the feed point to assure that the overhead vapor will separate into two liquid layers upon condensation.

The vapor from the first column is passed through a condenser and flows into a decanter vessel. The condensate separates into two distinct liquid phases in the decanter and the benzene-alcohol layer is continuously drawn off as reflux for the first column. The water layer, which settles on the bottom, is fed to a second column which strips any residual ethanol and recycles it to the condenser.

The first column functions almost exactly opposite to a normal distillation column. In this case the relative volatility of the water is higher so each plate below the feed serves to strip water from ethanol instead of vice versa. This allows essentially dry ethanol to be taken off the bottom of the first column.

The benzene circulates but it does not leave the system except for very minor losses with the ethanol exiting column 1 and in the water exiting. This is significant for two reasons: (1) the benzene does not have to be replenished very often and (2) the benzene, which is considered a dangerous chemical, can be confined and controlled.

Not every agent used to "break the azeotrope" will perform the same way as benzene. With some azeotropic systems the overhead vapors cannot be separated into two distinct liquid layers. A third type of distillation called extraction is needed to separate the agent and the ethanol from the water. Similarly, not every agent increases the relative volatility of the water present. Greatly increased energy for the azeotropic distillation is needed to evaporate 95% of a mixture than to evaporate 5% of it.

2. Dessicants

Some chemicals react with water to form a stable compound but do not react with ethanol. One such compound is calcium oxide, CaO. Passage of an ethanol-water mixture through a finely divided bed of CaO will remove one molecule of water for every molecule of CaO present. If more water is present than the CaO can react with, the water will be drawn off with the ethanol. Caution is advised because the reaction of CaO and H_2O gives off a great deal of heat.

The hydrated lime which results can be converted back to CaO by heating in a lime kiln. The energy given off during the reaction producing the lime as well as the activation energy required to start the regeneration reaction must be supplied by the kiln.

Research by Ladisch of Purdue University indicates that cornstarch may also prove to be a good dessicant. Development of this novel process to use cornstarch is being continued under his guidance.

3. Molecular Sieves

There are materials called synthetic zeolites that can differentiate between chemical compounds on the basis of their molecular size. For purposes of illustration, the system can be described as a matrix of "big holes" and "small holes". The "big holes" allow the mixture to flow through the zeolite material. The "small holes" lead to chemically reactive sites in the zeolite molecules. The small holes are only 3 Angstroms across (an Angstrom is 10-24 centimeters and is roughly the diameter of an atom). A molecule of water is less than 3 Angstroms across; a molecule of ethanol is more than 3 Angstroms across. Thus, the water molecules can be absorbed on the reactive sites of the zeolite but the ethanol cannot.

When all of the reactive sites in the zeolite are occupied, the water comes through the bed with the ethanol. This point is called "breakthrough" and requires switching to another bed of synthetic zeolite if operations are to be continued.

Water-saturated zeolite material can be regenerated by heating it with a hot dry gas. Because the zeolite can to some extent react with oxygen, use of a nonoxidizing gas such as nitrogen or carbon dioxide is usually preferred. Large volumes of gas are required to regenerate a molecular sieve and the gas must be very dry in order to remove the water from the zeolite. The amount of heat supplied must be greater than the heat of absorption given off when the water reacts with the zeolite.

4. Membrane Technology

The energy input for distillation could be reduced substantially through the use of membranes. The membrane would act as a filter to separate the water from the ethanol molecules. Depending on the type and quality of membrane, either partial separation may be accomplished or complete separation may be obtained. Sulfonic acid-based membranes appear to hold the most promise at the present time as research continues.

II. Denaturing of Ethanol

The Bureau of Alcohol, Tobacco, and Firearms requires that all fuel ethanol be completely denatured before removal from the site on which it is produced. Denaturing is accomplished by transferring a specific quantity of ethanol from the product hold tank to the denaturing tank and by mixing in a prescribed quantity of denaturant.

Regulations permit the use of five gallons or more of the following substances in every 100 gallons of alcohol for rendering it unfit for beverage purposes and eligible for removal from the plant free of the Federal Exise Tax on alcohol:

A. Gasoline
B. Kersosene
C. Deodorized Kerosene
D. Rubber Hydrocarbon Solvent
E. Methyl Isobutyl Ketone
F. Mixed Isomers of Nitropropane
G. Any combination of the above

III. Ethanol Storage and Handling

Any normal storage vessel sized to the plant's production capacity will suffice. If dry or anhydrous ethanol is produced, the utmost care must be exercised to prevent it from picking up moisture from the air. Normally, fuel tanks are vented to allow gases to escape without pressurizing the tank. Dry ethanol can be stored indefinitely in tanks that have been equipped with an air-tight bladder. The bladder can expand and contract as necessary to allow for heat expansion and cold contraction and at the same time keep out moisture.

IV. Stillage Treatment

The stillage produced can be (1) fed wet to animals, (2) dried for animal feeding, (3) processed to recover protein for human consumption, (4) applied to soil as as amendment or (5) disposed in an environmentally acceptable manner.

A. Feeding Wet Stillage

When grain stillage comes out of the bottom of the beer still it is a hot liquid of approximately 90% water and 10% nonfermentable solids. The water contains a minor quantity of soluble proteins, a variety of organic acids, some aldehydes, and unconverted sugars. The nonfermentable solids are about one-third protein and the remainder are comprised of unconverted starch, fibrous material, and grain husks.

Generally, the nonfermentable solids are separated from the liquid by passing over a slant screen or running through a centrifuge. The liquid removed is called thin stillage and the nonfermentable solids are called distiller's grains if the original substrate was grain. The thin stillage represents a pollution load of about 30,000 mg/l BOD (biochemical oxygen demand[g]) and it must either be evaporated or treated in a sewage treatment facility.

The distiller's grains are often run through a press to remove more of the water. After they exit the press they still contain about 60% moisture although they feel dry to the touch. In this form, distiller's grains are very susceptible to spoilage by anaerobic and aerobic microbes because the residual sugars are an excellent energy source. Generally, the grains must be fed within 24 to 48 hours after they are generated or molds will render them unfit for consumption.

Wet grain stillage is a good protein supplement for dairy cattle and beef cattle. One cow can consume each day the stillage dry matter from about one gallon of ethanol production. Thus, the stillage from a 1,000-gallon-per-day ethanol plant would require about 1,000 cattle to consume it.

A problem with feeding wet stillage is the fact that an animal can consume no more than exceeds its normal daily water intake, or diarrhea results. The animal's energy needs must be met and its amino acid complement must be satisfied every day. Last and probably most important, the animal must like to eat the stillage (palatability). Tables V-8,9 show typical analysis for corn stillage and Table V-10 shows theoretical values for the stillage obtained from various other substrates.

TABLE V-8

TYPICAL ANALYSIS OF DISTILLERS' DRIED GRAIN SOLIDS - CORN

	Distillers' Dried Grains (%)	Distillers' Dried Solubles (%)	Distillers' Grains with Solubles (%)
Moisture	7.5	4.5	9.0
Protein	27.0	28.5	27.0
Lot	7.6	9.0	8.0
Fiber	12.8	4.0	8.5
Ash	2.0	7.0	4.5
Amino Acids			
Lysine	0.6	0.95	0.6
Methionine	0.5	0.5	0.6
Cystine	0.2	0.4	0.4
Histidine	0.6	0.63	0.6
Arginine	1.1	1.15	1.0
Aspartic Acid	1.68	1.9	1.7
Threonine	0.9	0.98	0.95
Serinine	1.0	1.25	1.0
Glutamic Acid	4.0	6.0	4.2
Proline	2.6	2.9	2.8
Glycine	1.0	1.2	1.0
Alanine	2.0	1.75	1.9
Valine	1.3	1.39	1.3
Isoleucine	1.0	1.25	1.0
Leucine	3.0	2.6	2.7
Tyrosine	0.8	0.95	0.8
Phenylalanine	1.2	1.3	1.2
Tryptophan	0.2	0.3	0.2

TABLE V-9

ENERGY CONTENT FOR FEED

	Distillers' Dried Grains (%)	Distillers' Dried Solubles (%)	Distillers' Grains with Solubles (%)
For Cattle:			
Total digestible nutrients	83	80	82
Megacalories per kilogram	2.19	2.32	2.3
For Poultry:			
Megacalories per kilogram	2.0	2.75	2.62
For Swine:			
Megacalories per kilogram	1.84	2.98	3.39

TABLE V-10

Feedstuffs	Moisture	Crude protein	Ether extract	Crude fiber	Ash	Nitrogen-free extract	Calcium	Phosphorus	Carotene	Thiamine	Riboflavin	Niacin	Pantothenic acid	Choline
	Percent	Percent	Percent	Percent	Percent	Percent	Percent	Percent	mg-lb.	mg-lb.	mg-lb.	mg-lb.	mg-lb.	mg-lb.
Brewers' dried grains:														
18-23 percent protein	7.9	20.7	7.2	17.6	4.1	42.5	0.16	0.47	......	......	0.6	31.5	......	......
23-28 percent protein	7.7	25.4	6.3	16.0	4.3	40.3	.16	.47	......	......	......	......	......	......
Distillers' dried grains:														
Corn	6.0	27.6	8.7	12.5	2.4	42.8	.10	.45	0.8	0.7	1.3	17.4	2.7	74
Milo	6.9	40.8	13.1	11.8	1.6	25.8	....	....	......	.3	1.3	25.0	2.6	79
Rye	6.5	20.9	6.4	14.4	2.3	49.5	....	....	......	.7	1.8	8.9	2.6	......
Wheat	7.0	30.4	6.6	13.4	2.2	40.4	.06	.42	.5	.8	1.8	33.2	3.1	......
Distillers' dried grains with solubles:														
Corn	7.3	29.1	9.0	9.5	3.8	41.3	....	....	.5	.8	3.0	36.5	5.0	206
Milo	4.2	32.8	9.7	12.1	3.7	37.5	....	....	......	.6	2.0	28.0	5.7	141
Rye	....	....	....	....	....	....	....	....	......	......	3.8	......	......	......
Wheat	7.4	32.9	5.6	9.4	4.8	39.9	.15	.68	1.1	......	5.6	......	......	......
Distillers' dried solubles:														
Corn	7.2	27.4	7.6	4.3	7.5	46.0	.43	1.30	.3	3.2	6.1	64.5	10.4	339
Milo	6.9	29.4	5.9	3.5	7.7	46.6	....	....	......	2.2	4.9	60.0	11.1	352
Rye	6.5	35.5	.5	2.4	7.8	47.2	....	....	......	1.2	6.3	18.7	14.1	......
Wheat	7.5	30.1	2.0	8.0	3.0	50.4	.35	1.51	1.0	3.0	5.3	103.5	17.5	......
Distillers' (potato) dried resudue	3.9	25.9	4.1	13.0	7.4	45.7	....	....	......	......	......	......	......	......
Fermentation solubles:														
Grain	7.3	35.8	6.2	8.1	6.2	36.4	....	....	......	......	......	......	......	......
Molasses	4.5	28.0	1.2	1.8	12.6	51.9	....	....	......	......	......	......	......	......
Malt sprouts	7.2	24.6	1.8	13.9	7.5	45.0	....	....	......	......	5.5	25.4	......	......
Yeast, brewers' dried	5.5	47.2	.9	3.0	7.3	36.1	....	....	......	31.2	14.1	216.7	50.0	......
Yeast, feed, dried	6.0	52.6	4.3	17.2	7.7	12.2	.07	1.55	......	10.0	30.0	159.0	......	......

B. Drying and Feeding Dry Stillage

To give grain stillage a storage and transport life without spoiling, drying is usually required. This is done by dewatering as in the previous case, but the nonfermentable solids are then sent to a drum dryer. The thin stillage is sent to an evaporator for concentration and then returned to the drum dryer to be combined with the grains. The product is called distiller's dried grains with solubles (DDGS), or distiller's dark grains. This product is slightly higher in total protein than the wet grains because the soluble proteins have been recovered. With the exception that water intake is no longer being a major concern, distiller's dried grains can be fed with the same or greater effectiveness than wet grains.

C. Protein Recovery for Human Consumption

If a market develops for human consumption of protein from distiller's grains, these proteins could be recovered by specialized centrifugation. Presently, no domestic market exists and test marketings have met with dismal response. Many reports show research is being done in this area.

D. Application as a Soil Amendment

Whole stillage has a pH that ranges from 5.0 down to about 2.0 if the batch has gone sour. Application to basic soils can serve to adjust pH toward neutral, greatly reducing the amount of nitrogen fertilizer which must be added to the soil. If whole stillage is added to acidic soils, it will compound a problem that already exists.

Stillage contains important quantities of organic nitrogen, phosphorus, and potassium although the concentrations are not comparable to those for commercial fertilizers.

Because of the high protein value of the nonfermentable solids, land application of these as expected will be a disposal method of last resort. The thin stillage has much less value and its routine return to the soil with irrigation water is very probable. If this method is used, caution should be exercised to determine if the acidity will be harmful to any components of the irrigation system.

E. Environmentally Acceptable Disposition

Although it is currently inconceivable that no valuable use could be found for stillage, any stillage which must be disposed should be done in a way that is not harmful or offensive to people or to the environment. Anaerobic digestion can be used to effectively reduce the mass of material and at the same time generate methane gas to burn. The sludge that results can be aerobically treated in a sewage treatment system and reduced to carbon dioxide and water.

V. Culturing Enzymes and Yeast

The enzymes for converting starch to simple sugar can be obtained by a process called malting. Malting is the germination of barley during which the desired enzymes are formed, and is generally conducted in three stages. In the first stage, called steeping, clean barley is soaked in water until the desired moisture content is raised from about 11% to between 44% to 48%. In the second stage, called germination, the steeped barley is grown under controlled conditions. In the third and final stage, the germinated barley is dried in a current of hot air to arrest further growth.

Steeping is usually done in vertical cylindrical tanks with steep conical bottoms for proper drainage. Clean barley is transferred from storage to these tanks and water between 41° F and 65° F is added. The time required to attain the desired "steep-out" moisture content depends upon the water temperature, kernel size, barley variety, and protein content. The warmer the steeping water the more rapid the rate of water absorption, but temperatures in excess of 65° F are to be avoided because of the lack of entrained and dissolved oxygen and the potential for growth of undesired microorganisms.

Water is usually drained and changed every six to eight hours. Aeration must be supplied to the tank to provide oxygen for barley respiration.

Steeping often requires 45 to 50 hours to reach desired moisture content. Steeping usually is stopped when the grain has just begun to "chit," the first appearance of rootlets.

Germination is accomplished after allowing the steeped barley to "rest" in warm dry air. Commercial germination is accomplished by transferring steeped barley to a compartment with a perforated metal floor. Humid air between 52° F and 60° F is passed through the bed. A screw conveyor keeps the rootlet masses broken up and mixes the malt.

Germination is stopped by drying the malt with hot dry air in a process called kilning.

Fungal amylase enzymes can be directly cultured by growth of molds of the genus Aspergillus. The strain Aspergillus niger produces both dextrinizing and saccharifying enzymes. Aspergillus niger can be grown in a medium of thin stillage containing 2% by weight corn meal and 0.5% by weight calcium carbonate. After three to five days of growth with continuous aeration, the culture liquor obtained is a satisfactory substitute for malt.

The process of yeast propagation from a seed culture to volumes sufficient for desired fermentation rates is merely a progression of cultures of increasing size. Usually the pure yeast culture propagation plant consists of three stainless steel vessels which are located in a separate room that can be kept scrupulously clean. The vessels are equipped with jackets for heating and cooling, sight glasses, and a venting system to remove external unsterilized air.

The propagation equipment including all valves, filters, pipes, and vessels, is thoroughly cleaned and sterilized between batches to prevent growth of any undesirable microbes.

The second step of the process is the transfer of a portion of the master culture kept in a sterile yeast bank to a series of individual 200 milliliter flasks containing 100 milliliters of sterilized glucose solution. After two days of incubation at 25° C, the 100 ml sultures are microscopically examined and the flasks which exhibit vigorous normal cell growth are used for propagation in larger volumes of sterile wort. The next larger propagation step is performed in 1,000 milliliters of sterile wort contained in a 2,000 milliliter flask. Again the incubation is carried out for two days at 25° C and the yeast is reexamined. The contents of the 2,000 milliliter flasks are used for inoculation of the propagation plant. When not needed these can be stored for up to three weeks at 39° F as a stock culture, ready to be used for inoculation.

The first propagation stage takes place in the small propagation vessel which contains about 50 liters of sterile aerated wort. Through a special valve, between one and five liters of the laboratory inoculum are introduced and mixed with the wort by a gentle stream of sterile air. At the height of fermentation (high Kraeusen), the content of this vessel is transferred as inoculum into a larger vessel containing 500 liters of sterilized aerated wort. In this way the lag phase is avoided and vigorous fermentation proceeds without interruption.

If 500 liters is sufficient for pitching requirements, the propagation is carried no further and the wort is held for the next fermentation. If this quantity is insufficient for pitching, the contents of the second propagator are transferred to a still larger vessel containing 4000 liters of sterilized aerated wort and the process is repeated.

The introduction of pure oxygen into the propagator greatly reduces propagation times. The presence of sufficient yeast nutrients, including magnesium, calcium, potassium, phosphate, nitrogen, and trace mineral, is an absolute requirement. The presence of excess quantities of metal ions, particularly iron and copper, is detrimental to proper growth.

VI. Maintenance

Maintenance activities can be divided into two categories: routine maintenance and repairs. The purpose of routine maintenance is to prevent breakdowns by checking potential failure points, and greasing and lubricating moving parts.

A. Routine Maintenance

Every pump, motor, valve, and seal in the plant should be checked at least once each day. A checklist is an essential item for assuring that each component receives the appropriate routine maintenance. The checklist should not contain items that have minimal maintenance requirements.

B. Repairs

Some breakdowns must be anticipated as a natural course of operation. Although the exact component that fails and the exact time that it fails cannot be predicted, the items with a high potential for failure can be identified. An annual capital reserve should be maintained equal to 5% of the total purchase price of installed pumps, motors, controllers, valves, and seals.

VII. Safety

An ethanol production facility harbors many hazards. A person acquires a working knowledge of "do's" and "don'ts" as the system becomes more familiar, but there is also a tendency towards recklessness and carelessness that grows with time. The initial cautions which this section contains may prevent injuries in early operating stages, but unless proper procedures are part of the work routine, serious and unnecessary accidents will occur.

A. Overall Considerations

Safety procedures protect not only people but equipment as well. The "it'll heal" rationale for taking personal risks does not apply to equipment. This is not to imply that all procedures protect equipment or that equipment should be a first concern. However, the benefits of safe work habits extend beyond the protection of life and limb. See Tables V-11 for additional information.

B. Fire Hazards

The following are general guidelines for fire prevention/hazards:

1. Cabinets, shelves, lockers, and partitions for storage of highly flammable materials should be constructed of noncombustible materials such as slate or steel.

2. Flammable liquids should be stored in non-combustible containers.

3. Maintain a daily schedule for collection and disposal of combustible waste.

4. Do not store any combustible materials in the immediate proximity of heating devices and electrical devices.

5. Ethanol samples and product should be stored in properly vented containers. Ethanol is less volatile than gasoline which forms an equilibrium vapor that is too rich to burn, so the vapor above store ethanol is potentially explosive.

6. Dust, especially grain dust, is highly combustible and potentially explosive. Make every attempt to confine its spread.

7. Do not smoke near the distillation system, condenser, pumps and product tank, or during transfer of ethanol to transportation vehicles. NO SMOKING signs should be posted conspicuously in these areas.

8. Lubricants should be stored in self-closing metal containers.

9. Fire extinguishers for electrical fires and for chemical fires should be kept in conspicuous and readily accessible positions. Their locations should be indicated with signs and they should be periodically checked to insure proper function.

10. Fire doors, exits, and walkways should be kept clear.

11. Flammable liquids should not be stored in glass or plastic containers. (Liquids are considered flammable if their flash point is less than 200° F such as ketones, petroleum spirits, alcohols, and oil-base products.)

There are three classes of fires which are likely to occur in an ethanol production facility and each should be combatted using specific techniques. A Class A fire is one burning ordinary combustible materials such as wood, paper, and rags. A Class B fire is one burning paints, oils, propane, acetylene, gasoline, acetone, and alcohol. A Class C fire is one burning materials connected to electrical circuitry. Once the electrical current is turned off, the remaining fire is either Class A or Class B or a combination of both. Class D fires are burning flammable metals such as magnesium, titanium, or sodium. Since it is very unlikely that these will ever be present in an ethanol production facility, there will be no further discussion of Class D fires.

Class A fires can be combatted using water, and in fact, Class A fire extinguishers are pressurized cannisters containing water. Carbon dioxide fire extinguishers are used only on Class B and C fires and are operated by directing the discharge horn at the base of the flame while depressing the discharge valve.

A CO_2 fire extinguisher is most effective when used indoors. Wind or air currents quickly disperse inert gas and render it ineffective as a fire retardant.

Dry chemical extinguishers are also for use on Class B or C fires only. Operation requires removal of the locking pin and puncturing the cartridge.

In general, when fighting a fire, a person should keep "upwind" of the blaze. Even indoor fires cause so much gas expansion that the direction of draft literally becomes an indoor wind. Avoid breathing smoke to the extent possible but never attempt to combat a blaze without a fresh air respirator if toxic fumes are being produced.

Expended fire extinguishers should be placed well out of the path of travel and in a horizontal position. Water should never be used on an electrical fire because of the danger of conduction along the water stream. Water should not be used to extinguish chemical fires largely because many are immiscible in water and the water merely serves to spread the fire.

Carbon dioxide fire extinguishers have internal pressure greater than 850 psi, depending upon the temperature, and should be handled with the same care given to other compressed gas cylinders. When directing the flow of CO_2, only the insulated portion of the discharge horn should be held to prevent static shock and frostbite.

C. Explosion Hazards

An explosion is merely extremely rapid combustion accompanied by a compression shock wave. Explosions rarely occur in undispersed flammable solids or liquids because the rate of flame propagation is too slow. Generally explosions occur in airborne combustible dust or in mixtures of combustible gases and air. Obviously, explosions cannot be combatted once initiated because they occur so rapidly that event is done before any possible reaction. Thus, efforts must concentrate on prevention. Among the precautions to prevent explosions are:

1. Keep grain dust swept off of surfaces and properly disposed as part of daily housekeeping routine.

2. Keep ethanol storage tanks cool and removed from ignition sources.

Another type of explosive event is the rupture of a pressurized vessel. This can occur if heated steam is confined in a vessel with no high pressure relief. In general, systems that require normal operating pressures greater than 15 pounds per square inch above ambient, require the operator to be specially licensed.

D. Handling of Cleaning Solvents

There are literally thousands of cleaning solvents and many can be used interchangeably. Where possible, the less hazardous solvents should be substituted for hazardous materials. The hazards from solvents include inhalation, ingestion, skin absorption, fire, and explosion. When purchasing solvents consideration should be given to:

1. Toxicity, especially the consequences of exposure in terms of response to odor, effect on performance, irritation to eyes and nose, and others.

2. Flammability and volatility (vapor pressure).

3. Effectiveness for the cleaning operation.

4. Conditions for use.

The least toxic, least flammable, least volatile solvent that will do the job should be selected. No one solvent has all the desirable characteristics for every job. Therefore, the selection should be based on careful compromise to achieve the intents of the above consideration. Generally solutions of detergents are preferred to other chemical solvent.

If detergents will not adequately perform the required cleaning tasks, so-called "safety solvents" can be used. These include 1,1,1 trichloroethane, dichloromethane, paraffins, and napthas with high flash points. All solvents including these, require good ventilation during use.

Moderately hazardous solvents include toxic solvents like trichloraethylene, dichloroethane, dichloroethylene, and chloroform (trichloromethane); flammable solves such as ethanol, isopropanol and butanol; and substances that are both toxic and flammable like turpentine, toluene, and xylene.

Very hazardous materials include highly toxic solvents like carbon tetrachloride and tetrachoroethane; highly toxic and also flammable substances such as carbon disulfide, benzene, and methanol; and highly flammable as well as toxic materials like methyl acetate, ether, acetone, or gasoline.

Solvents should be stored in properly labeled containers suitable for the hazards associated with the contents. Nonaqueous solvents should be stored in well-ventilated areas away from heat flames or electrical arcs.

When using cleaning solvents, skin contact should be avoided if possible. Gloves should be worn and eyes should be covered with face shields or goggles.

Smoking should be prohibited in areas where solvents are in use, and portable signs should be conspicuously displayed to indicate use. If solvent is spilled on clothing, it should be immediately removed to prevent skin absorption.

E. Toxic Materials Encountered

Most materials have some degree of toxicity, inasmuch as toxicity is a function of the quantity of material ingested or inhaled, the mechanism of effect on the body, and the significance of the effect. Since there are a vast number of toxic materials, this discussion is confined to those that are most likely to be used in ethanol production.

Any toxic material should be stored in a clearly marked individual container that indicates both its poisonous nature and the appropriate remedy if ingestion or inhalation occurs.

Carbon tetrachloride and benzene should only be used within effect range of an exhaust hood.

Food and drinks should never be stored, handled, or consumed in areas where toxic materials are stored or used.

F. Handling of Acids and Bases

Concentrated acids and bases should be stored only in approved containers or closed glass vessels. Acids will corrode most mild metal containers rapidly enough to cause them to fail in an extremely short period of time.

Concentrated acids should be added to water or basic solutions very slowly with vigorous stirring to allow the heat of reaction to dissipate as hydrogen ions react with free hydroxide giving off energy.

Burns from hydrochloric acid, nitric acid, phosphoric acid, sulfuric acid, chlorine, and bromine should be washed with large quantities of water, then with a 5% solution of sodium bicarbonate (baking soda). In the case of severe or extensive burns, contact a physician as soon as possible.

Burns from concentrated base should be washed with large quantities of water.

If acids are taken internally, the mouth should be immediately rinsed with a 5% solution of sodium bicarbonate and the victim should be given milk or a suspension of 10 grams of magnesium oxide (magnesia) in 150 ml of water, or a mild solution of limewater and oil.

G. Burns

At any point during the operation of an ethanol plant, there are many vessels and pipes that have surface temperatures greater than 140^{o} F. These include the cooker, the heat source, the beer still, the rectification column, and all of the associated piping. Though all of these should be insulated to minimize heat loss, maintenance of these items is often attempted prior to allowing them to cool. First degree burns are indicated by reddening, and unless the burned area is extensive no direct treatment is required. Second degree burns are indicated by blisters and a sterile gauze should be applied to protect the wound from infection. Third degree burns are indicated by destruction of the tissue. These should be covered with a sterile gauze and a physician should be immediately contacted.

H. Vessel Entry Procedures

Cleaning of tanks and vessels often requires physical entry and manually scrubbing down the walls. Because the inside of a tank is a confined environment, sufficient oxygen may not be available to sustain life. Persons who die as a result of suffocation obviously cannot save themselves, and because tanks are opaque no one else will know of any difficulties unless posted as a tank watch at the access port.

Fermenters often contain CO_2 because it is generated during the fermentation process and is heavier than air. When the tank is emptied the CO_2 settles to the bottom and remains unless the tank is vented and purged with air. The CO_2 will desplace the available oxygen at the bottom of an unventilated tank to an extent sufficient to cause suffocation.

The following procedures should be followed when preparing to enter a tank:

1. Open the access ways and purge with air.

2. Force ventilation by using fans or blowers.

3. Lock out all electrical connections to agitators or mechanical equipment in the tank to prevent inadvertent start-up by someone unaware of anyone's presence in the tank.

4. Lock-close all valves for steam, water, or chemical input to the tank. Padlocks should be used--not bolts or wire which can be easily removed by others.

5. Post a tank watch at the entry position.

6. Provide a safety rope--firmly attached--so the tank watch can retrieve a person in the event of an accident. (Table V-11)

I. Lock-Out of Mechanical and Electrical Equipment

Prior to servicing pumps, motors, drives, gearboxes, or any moving machinery, disconnect the power source and lock-out. All disconnect boxes approved for use by the Under-writers Laboratory have provision for lock-out with padlocks. The danger to life and limbs while servicing moving machinery not only warrants lock-out of the power supply but also blocking rotating shafts appropriately to prevent any turning.

J. Preparing for Maintenance

Often equipment is hoisted into position by block and tackles anchored to any available overhead support. Process piping, instrumentation lines, electrical cable trays, and electrical conduit should never be used for this purpose. None of these is designed to bear the additional load of becoming the principal transfer support for other components.

TABLE V-11 - ETHANOL PLANT HAZARDS

Hazards	Precautions
1. Overpressurization; explosion of boiler	* Regularly maintained/checked safety boiler "pop" valves set to relieve when pressure excedds the maximum safe pressure of the boiler or delivery lines
	* Strict adherence to boiler manufacturer's operating procedure.
	* If boiler pressure exceeds 20 psi, acquire ASME boiler operator certification. Continuous operator attendence required during boiler operation.
2. Scalding from steam gasket leaks	* Place baffles around flanges to direct steam jets away from operating areas.
	* (Option) Use welded joints in all steam delivery lines.
3. Contact burns from steam lines	* Insulate all steam delivery lines.
4. Igniton of ethanol leaks/ fumes or grain dust	* If electric pump motors are used, use fully enclosed explosion-proof motors.
	* (Option) Use hydraulic pump drives; main hydraulic pump and reservoir should be physically isolated from ehtanol tanks, dehydration section, distillation collumns, condenser.
	* Fully ground all equipment to prevent static electricity build-up.
	* Never smoke or strike matches around ethanol tanks, dehydration section, distillation columns, condenser.
	* Never use metal grinders, cutting torches, welders, etc. around systems or equipment containing ethanol. Flush and vent all vessels prior to performing any of these operations.

TABLE V-11 - ETHANOL PLANT HAZARDS (con'd)

Hazards	Precautions
5. Handling acids/bases	* Never breathe the fumes of concentrated acids or bases. * Never store concentrated acids in carbon steel containers. * Mix or dilute acids and bases slowly-allow heat of mixing to dissipate. * Immediately flush skin exposed to acid or base with copious quantities of water. * Wear goggles whenever handling concentrated acids or bases; flush eyes with water and immediately call physician if any gets in eyes. * Do not store acids or bases overhead work areas or equipment. * Do not carry acids or bases in open buckets. * Select proper materials of construction for all acid or base storage containers, delivery aides, valves, etc.
6. Suffocation	* Never enter the fermenters, beer well, or stillage tank unless they are properly vented.

K. Housekeeping

All the aesthetic values which are attendant to a clean, orderly work place are secondary to the prevention of stumbling and falling injuries. This type of injury is one of the most common and serious injuries that occurs in an operating facility. The admonition "pick up after yourself" has merit measurable in a spectrum of toes that do not get stubbed to bones that do not get broken.

Aside from sheer aesthetic value, there are important reasons for maintaining a clean and orderly working area. Grain dust must be controlled because it poses the hazard for both explosion and fire. Dirt, chaff, and the like are ideal for harboring unwanted microbial contaminants. Tools and equipment that are not properly stored after use are hazards to personnel and can be damaged themselves.

VIII. Bookkeeping Requirements

The Bureau of Alcohol, Tobacco, and Firearms requires that records of all transactions pertinent to alcohol production, sale, denaturation, and transport be maintained. The production records should include the material input to the fermenters, beer flow to distillation, ethanol proof and production rates, and rates of stillage generation. These records must be available for inspection by Bureau officers at any time. Permits must be present on-site for inspection.

IX. Ethanol as a Fuel for Internal Combustion Engines

Spark ignition and compression ignition engines are the predominant types of engines in use today, and are commonly termed gasoline or diesel engines. There are many differences in the operating and construction characteristics of these engines, but the most obvious is the method of fuel ignition. The gasoline engine uses an electric spark to initiate the rapid burning process, whereas the diesel engine relies on the heat generated in compressing air in the chamber to ignite the fuel. Different fuel properties are required to satisfy the operating characteristics of each type of engine.

Diesel engines are presently more fuel-efficient than gasoline engines and this type of engine is the predominant engine used in tractors and farm machinery. Some tractor manufacturers no longer offer gasoline engines. Gasoline engines with modified carburetion systems using natural gas for fuel are used as power units for irrigation pumping plants, and in Texas, energy used for pumping irrigation water is the largest single energy input to crop production. LP gas is also used as a fuel for gasoline engines.

Increasing fuel costs and questions about fuel availability makes an alternate fuel desirable for agricultural production. Ethanol derived from grain or other agricultural crops can be used as an alternate or supplemental fuel in spark ignition and diesel engines.

A. Engine Fuel Requirements

Ethanol does not meet the fuel specifications for either gasoline or diesel, but it is most suitable as a substitute fuel for spark ignition engines. Fuel specifications have been developed through more than 75 years of internal combustion engine development and the American Society of Testing and Materials (ASTM) has established test methods for specific properties. Several fuel properties, ASTM test method, and importance of the property for spark ignition engines are shown in Table V-12. Diesel fuel specifications are shown in Table V-13.

Typical fuel properties for ethanol and several other common fuels are shown in Table V-14. Two important observations can be made from comparing ethanol to gasoline and diesel:

1. The heat value per unit weight is less than gasoline or diesel.
2. The heat of vaporization is much higher than gasoline or diesel.

Compared to gasoline, ethanol contains about 61 percent as much energy per unit weight of fuel or about 65 percent as much energy per unit volume. This means that a little over 1.5 gallons of ethanol is needed to supply the same energy as that in a gallon of gasoline. There may be slight differences in conversion efficiencies, but an engine operating at 25 percent thermal efficiency on gasoline would have to operate at 37.5 percent efficiency to obtain a gallon for gallon fuel replacement. It is not possible to obtain this much of an increase without major engine modification. Diesel fuel has higher energy value than gasoline, and about 1.8 gallons of ethanol are needed to provide the same energy as a gallon of diesel.

Ethanol requires about 2.5 times more heat per unit weight for vaporization than gasoline. Considering that the heat value of ethanol is lower and more fuel is required, nearly 4.2 times more heat is required for fuel vaporization than is required for gasoline. In addition, ethanol is a single compound and vaporizes at a single temperature. Gasoline and diesel contain a variety of compounds which vaporize at different temperatures. About 10 percent of gasoline will vaporize at temperatures near 140° F, so it provides easier starting than ethanol in a cold engine.

Briefly summarized, when compared to gasoline ethanol has lower volatility, which makes engine starting more difficult, particularly at low temperatures. It has lower heat of combustion so volumetric fuel consumption will increase. Ethanol has a higher heat of vaporization which influences fuel-air distribution in combustion chambers; a slower flame speed which requires more spark advance; a higher octane or antiknock value which permits higher compression ratios and higher thermal efficiencies; and it has a different chemical composition which affects the stoichiometric air to fuel ratio. Ethanol also absorbs water which lowers its heat value and causes phase separation in gasoline-alcohol mixtures.

When comparing ethanol to diesel fuel, most of the comparisons given for gasoline are true, but because of its high octane rating, it has a low cetane number. This low cetane rating indicates that auto ignition is difficult to achieve and is the primary requirement for compression ignition engine fuels. This implies that the fuel must be modified for the engine or the engine modified to accept the fuel. Changing a diesel to spark ignition operation is one attractive option, but the compression ratio would need to be reduced to about 12:1, and this would eliminate multi-fuel use capabilities of the engine.

B. Engine Fueling Techniques and Performance

Ethanol use in internal combustion engines is not new. There are several techniques for using ethanol in internal combustion engines. Some require modifying the fuel to suit the engine and others require modifying the engine to suit the fuel. The predominant methods to use ethanol are:

1. Mixtures of ethanol and gasoline or diesel;

2. Vaporizing ethanol and mixing with intake air;

3. Direct injection;

4. Direct carburetion;

5. Dual fueling.

Various combinations of these techniques have been studied for both types of engines and some offer potential for replacing a significant percentage of fossil fuels.

C. Spark Ignition Engines

1. Gasohol

The predominant commercial ethanol fueling technique is a mixture of 10 percent anhydrous ethanol and 90 percent gasoline. Many tests have recently been made on gasohol-fueled vehicles and several concerns have been presented. Deterioration of fuel system components and phase separation of mixture are the primary concerns. Ethanol absorbs water and causes the phase separation to occur in mixtures. This is important because most alcohol made in on-farm stills will contain more water than can be tolerated by gasohol. Another concern reported has been difficult cold starting; but increased octane rating has more than offset these problems.

The most controversial aspect of gasohol use has been fuel economy. A 10 percent mixture of ethanol with gasoline reduces the heat value of the mixture about 3.5 percent as compared to gasoline. Most tests show that fuel economy per gallon of gasohol is about 2.5 to 3 percent less than gasoline; however, there are cases which show increases. These increases apparently come from changes in fuel air ratio changes resulting in a leaner mixture which was initially too rich. The engine under these conditions was not originally operating at peak fuel efficiency so the addition of the lower energy value ethanol automatically shifts the operating conditions to a more efficient point.

2. Straight Ethanol

Ethanol can be used as the only fuel in spark ignition engines through relatively minor changes in carburetor, manifold, and ignition timing. Fuel-jet size of carburetors must be increased to provide for increased fuel flow. Additional heat in the manifold may be required to obtain adequate vaporization of the fuel and good fuel-air mixtures. Starting aids such as a manifold heater or addition of a low volatile fuel will be needed for starting when temperatures are below about 50°F. Ignition timing needs to be advanced because of increased ignition delay time caused by ethanol properties.

To obtain greater efficiency when using ethanol, the compression ratio of most common gasoline engines should be increased. A spark ignition engine with a compression ratio of 12:1 operating on ethanol should obtain about 95 percent of the efficiencies commonly achieved by diesel engines. This ratio is probably too high for most gasoline engines, but the high octane ethanol can operate at this level.

D. Compression Ignition Engines

Ethanol is a poor fuel for diesel engines and major changes are required to either the engine or the fuel to use it as the sole fuel. Several techniques have been investigated, and most preserve the ability to operate in either a dual-fuel mode or with diesel alone.

1. Diesolhol

Anhydrous ethanol has been mixed with diesel fuel in blends up to 30 percent, but increased engine noise levels have been observed with as little as 10 percent ethanol. Blends of 10 percent ethanol and 90 percent diesel meet the specifications for diesel fuel, and thermal efficiencies remain essentially unchanged when loaded at 3/4 or full load. A slight decrease has been observed at light loads.

Two key problems have been observed with diesohol - phase separation and vaporization in the injector pump. Water in quantities as low as 0.13 percent can cause phase separation. A large percentage of the diesel fuel requires 350 - 400° F for vaporization, but at these temperatures the ethanol has already vaporized. This can occur within the injector pump or other parts of the fuel system and cause stoppages. Pressurizing or cooling parts of the fuel system may be required to control this action.

2. Fuel Additives

Several compounds have been used to increase the cetane number or auto ignition properties of ethanol. Most of these additives are highly explosive and dangerous to use. Amyl nitrate, cyclohexanol nitrate, ethyl nitrate, and acetone peroxide are a few of the ignition accelerators which have been tried but have not proven practical. One study showed that 10 percent cyclohexanol nitrate was required to improve ethanol to operate like diesel fuel. Lubrication of injector pumps is also of concern when using ethanol alone and additives may be needed for this purpose.

3. Direct Injection

Various methods for direct injection of ethanol into a diesel engine have been studied, but the self-ignition properties of ethanol have limited the success of this method. By increasing compression ratio in the 23:1 range, it may be possible to obtain auto ignition of ethanol, but even then some fuel additives will probably be needed. Some multifuel engines with compression ratio of 19:1 have been operated on 80-octane gasoline, but octane rating of ethanol is considerably higher than that.

Dual injection systems have been used to provide a small quantity of igniter fuel through one system and ethanol for the rest of the fuel through the other system. About the same results can be obtained through the easier technique of carbureting alcohol into the intake air. At present it appears that little potential exists for retrofitting diesel engines for direct injection of ethanol.

4. Dual-Fuel Operation

Carbureting--sometimes termed aspirating and fumigating--fuels into a diesel engine has been practiced for many years and is presently the technique showing the most potential for using ethanol in these engines. The ability to operate the engine on diesel is retained and can provide multifuel capability.

Tests show that approximately 56 percent of the energy for a diesel engine could be replaced with ethanol for a duty cycle common to farm tractors. The percentage of permissible alcohol varies with engine loading condition and maximum of 60-70 percent alcohol fuel occurred at about 50 percent of maximum torque. Percentage ethanol use decreased for lower or high torque.

Changes required for this type of operation include addition of a carburetor on the intake and readjustment of timing. A heater or heat exchanger may be required for enhanced vaporization of the carbureted ethanol. The injection timing for the diesel fuel must be advanced to obtain good ignition of the ethanol. Knock or misfiring is the factor limiting the amount of ethanol which can be used by this method. Engine runaway is possible with this technique unless provisions are made to close off the alcohol fuel supply which is being carbureted.

Others have injected alcohol into the intake air before it entered a turbocharger, and at least one commercial conversion kit is being offered for using alcohol by this technique. About 40 percent of the diesel energy use can be replaced with ethanol by this method. Thermal efficiency remains about the same except for some decrease at low loads.

Some researchers have used carburetion techniques, but injected vegetable oils instead of diesel fuels with the alcohol. In an open combustion chamber engine, they were able to use alcohol for 93 percent of the fuel requirement and vegetable oil for the remainder. With diesel fuel, a maximum of 74 percent of the fuel was supplied by alcohol. Use of the vegetable oils with alcohol allowed the engine to be overloaded from 60-65 percent higher thermal efficiencies occurred at those conditions. Vegetable oils were also used as the sole fuel and provide another agriculturally derived fuel alternative, but their long term effects have not been established.

5. Converting to Spark Ignition

Since ethanol is a better fuel for spark ignition engine operation, diesel engines can be converted to spark ignition operation. For ethanol, a compression ratio of about 12:1 should result in efficiencies of about 95 percent of the normal diesel engine efficiency, but most current diesel tractor engines are between 14 and 19:1. A conversion would depend on the particular engine but would probably require additons, replacement, or major modification to:

a. Pistons

b. Head Assembly

c. Intake Manifold

d. Ignition System

e. Carburetor

f. Governor

A major tractor manufacturer has used this approach and is presently field testing tractors in Brazil. It offers potential but retrofitting would eliminate multifuel capabilities.

6. Future Techniques

In addition to conventional fueling techniques, unconventional or "exotic" methods to best use alcohol are being studied. One such technique is the decomposition of alcohol into hydrogen and carbon monoxide, which are then used as the fuel. One concept is to use the exhaust waste heat and a catalytic reactor to convert alcohol to a hydrogen rich fuel. The concept would improve present internal combustion engine efficiencies 10-20 percent without any loss in power. This is achieved primarily through recovering much of the energy in the waste heat of the exhaust.

E. Exhaust Emissions

Exhaust emissions from internal combustion engines cannot be ignored, and several recent tests have been completed on gasohol powered vehicles. The data showed that gasohol:

1. Increased evaporative emissions by about 50%.
2. Decreased exhaust hydrocarbons about 9%.
3. Resulted in a net increase of exhaust plus evaporative hydrocarbon emissions.
4. Increased NO_x emissions by about 7%.
5. Decreased CO by about 35%.
6. Decreased fuel economy by about 2%.
7. Decreased volumeteric fuel economy (mph).
8. Increased fuel energy economy ($mi/10^5$ Btu).
9. Reduced CO, HC, and NO_x emissions at 20°, 45°, and 75° F.
10. Increased HC and NO_x emissions at 100° F.
11. Aldehyde emissions increased by about 25% at 20°, 75°, and 100° F.
12. Exhaust HC distribution not materially affected.
13. Road octane quality of an 81 RON fuel increased by 4.5 numbers and a 91 RON fuel by 3 numbers.

In general, use of alcohol fuels will not appreciably affect exhaust emissions except aldehydes.

X. Alternative Uses for Ethanol

Aside from trucks, automobiles, and tractors, there are some other pieces of equipment that might be operated on alcohol fuel. The conversion process for three non-vehicle pieces of machinery are as follows:

A. 4-Cycle Engines

Lawn mowers, implements, and pumps usually use single or multi-cylinder utility engines as their prime mover. The conversion process on these engines is uncomplicated, because the two metering jets on the carburetor are usually fully adjustable.

First, locate the main metering jet (this is the larger one with an oversize head) and open it (counterclockwise) about 1/2 turn. Then find the idle jet and open that screw between 1/2 and 3/4 turn (don't confuse this with the idle speed screw located on the throttle, which should be left alone). That's about all there is to it. Ignition timing is usually fixed on these engines, and can't be adjusted. A word of caution: If the exhaust fumes seem excessively hot--or the muffler starts to turn white--open the main jet slightly to enrich the mixture.

B. 2-Cycle Engines

Chain saws and some industrial engines are 2-cycle models. These will operate well on alcohol by either (1) opening the main jet and idle jet as described in the 4-cycle section (most 2-strokes also have fully adjustable jets), or (2) as an alternative, purchasing a carburetor made specifically for alcohol use. These are also adjustable and are usually used for racing purposes when the engines are applied to go-carts or motorcycles. The main difference between the alcohol and gasoline carburetors is that the alcohol models provide for increased flow.

When operating a 2-stroke engine on alcohol, synthetic oil must be used in the fuel, since petroleum-based oils do not mix well with alcohol. Typical product names are Neo, Klotz, Amsoil, and S.O.F.-7.

C. Gun-Type Oil Burners

It is also possible to utilize alcohol in a home heating furnace or water heater, and the adjustment is fairly straightforward. First, partially shut off the burner air supply by turning the air inlet valve down. This valve is located right on the burner and usually has a marking needle indicating an adjustment scale of 1 through 10. If the heat provided by this simple adjustment is not sufficient, it may be necesary to go to a larger nozzle. Metering nozzles are available in several different gallon-per-hour rates, and they can be purchased inexpensively from a local plumbing and heating supplier.

TABLE V-12 - GASOLINE SPECIFICATIONS

Property	ASTM Test Method	Importance
Volatility		
Distillation	D 86	Cold weather driveability; carburetor icing; hot start and drivesway; vapor lock; carburetor evaporation losses; deposits in crankcase, combustion chambers, and spark plugs.
Vapor-to-Liquid Ratio	D 2533	Vapor lock.
Vapor Pressure	D 323	Low temperature starting; fuel tank evaporative losses; vapor lock.
Antiknock Performance		
Research Octane No.	D 2699	Low to medium speed knock; after run.
Motor Octane No.	D 2700	High speed knock; part throttle knock.
Corrosivity	D 130	Fuel system durability.
Stability		
Existent Gum	D 381	Induction system deposits.
Oxidation Stability	D 525	Storage life.
Sulfur Content	D 2622	Exhaust emissions; engine depostis and wear.
Antiknock Additives	D 2599	
Lead Content	D 3229	Catalyst deterioration.
Manganese Content	D 3237	Engine hydrocarbon emissions; oxygen sensor deterioration.

TABLE V-13 - DIESEL FUEL SPECIFICATIONS (ASTM D 975)

	No. 1	No. 2
Flash Point, °F, Min.	100	125
Water & Sediment, Vol. %, Max.	0.05	0.05
Carbon Residue 10% Btm. %, Max.	0.15	0.35
Ash, Wt. %, Max.	0.01	0.01
Distillation, 90% Point, °F	550 Max.	540-640
Viscosity at 100°F, CSt	1.3-2.4	1.9-4.1
Sulfur, Wt. %, Max.	0.50	0.50
Copper Strip Corrosion, Max.	No. 3	No. 3
Cetane No., Min.	40	40

Source: R. L. Courtney and H. K. Newhall. 1979.

Typical fuel properties for ethanol and several other common fuels are shown in Table 3. Two important observations can be made from comparing ethanol to gasoline and diesel:

1. The heat value per unit weight is less than gasoline or diesel;
2. The heat of vaporization is much higher than gasoline or diesel.

TABLE V-14

COMPARISON OF FUEL PROPERTIES

	Ethanol	Methanol	Natural Gas	Propane	Gasoline (Regular)	No. 1 Diesel	No. 2 Diesel
Chemical Formula	C_2H_5OH	CH_3OH	--	C_3H_8	--	--	--
Heating Value Higher (Btu/lb)	12,800	9,600	24,100	21,680	20,300	19,600	19,500
Btu/gal (Higher)	84,700	63,580	1,085*	92,140	124,100	135,250	138,750
Heat of Vaporization (Btu/lb)	396	502	--	147	142	115	105
Specific Gravity	0.794	0.797	--	0.51	0.73	0.83	0.85
Research Octane	106	98	--	115	85-94	--	--
Motor Octane	99	--	--	97	77-86	--	--
Cetane Number	-20 to 8	--	--	--	10 to 20	45-55	40-50
Stoichiometric Mass Air/Fuel Ratio	9.0	6.5	17.3	15.7	14.7	16	16

APPENDIX A

PARTIAL LIST OF ENZYME SUPPLIERS

Biocon (U.S.) Inc.
261 Midland Avenue
Lexington, Kentucky 40507
(606) 254-0517

Enzyme Development Corporation
210 Plaza
New York City, New York 10001
(212) 736-1580

Fermco Biochemicals, Inc.
2638 Delta Lane
Elk Grove Village, Illinois 60007
(312) 595-3131

G. D. Fermentation IND Corporation
1 North Broadway
Des Plaines, Illinois 60016
(312) 827-9700
Jim Zieger

Miles Laboratories, Inc.
Enzyme Products Division
P.O. Box 932
Elkhart, Indiana 46515
(219) 262-7176
James P. Wachter

Natick Laboratories Development Center
Pollution Abatement Division, U.S. Army
Natick, Massachusetts 01760
(617) 653-2914
Leo A. Spano
(cellulose enzymes and information only)

Novo Labs
59 Danbury Road
Wilton, Connecticut 06897
(203) 762-2401
Jim Crawford

Rohm & Haas
Independence Mall West
Philadelphia, Pennsylvania 19105
(215) 592-2517
Bob Broadbent

Schwarz Service International Ltd.
230 Washington Street
Mt. Vernon, New York 10551
(914) 664-1100
Mr. Aberdein

APPENDIX B

CONVERSION FACTORS

1 gallon water = 8.33 pounds (at 60° F) = 0.134 cubic foot = 128 fluid ounces = 4 quarts = 8 pints = 3.785 liters

1 gallon of ethanol weighs 6.6 pounds

a barrel of crude oil = 42 gallons

1 Btu = 252 calories = heat required to raise 1 lb of water 1 degree Fahrenheit (°F).

1 bushel = 56 pounds

1 calorie = 0.00397 Btu = heat required to raise 1 gram of water 1 degree Centigrade (°C).

1 U.S. liquid gallon = 4 quarts = 231 cubic inches = 3.78 liters

8 gallons = 1 bushel

1 liter = 1.057 U.S. liquid quarts

1 fluid ounce = 30 milliliters

1 pound = 453.6 grams

1 cubic foot = 7.48 liquid gallons = 62.36 pounds H_2O (at 60° F)

1 acre = 43,560 square feet = 4,840 square yards

To convert from °F to °C, subtract 32 and then multiply by 5/9.

To convert from °C to °F, multiply by 9/5 adn then add 32.